Devansh
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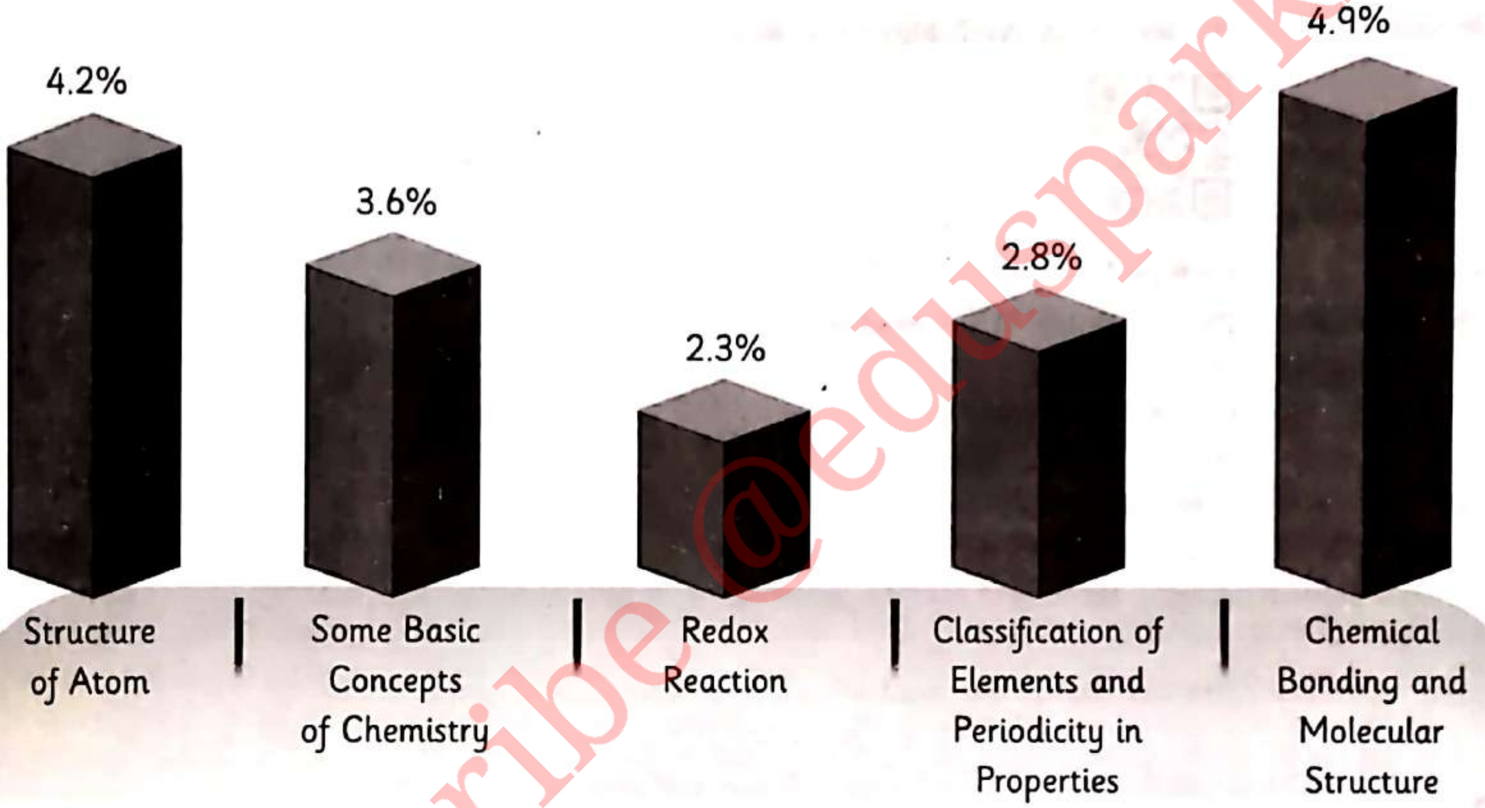

Chapter Wise Weightage (in %) Based on Past 6 Years JEE Main Papers

CHEMISTRY
Module 1

Resilience: In this module for the emotional well being we will practice resilience along with our regular academic learning

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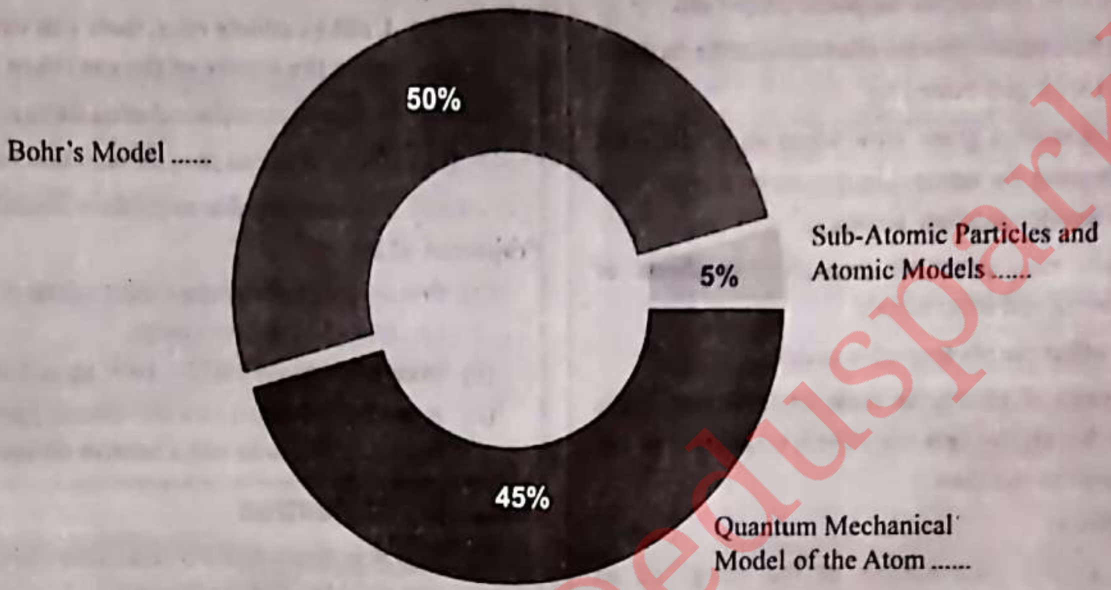
CHAPTER 1

Structure of Atom

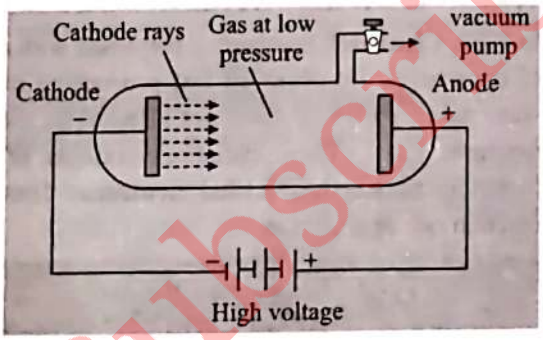
Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

FUNDAMENTAL PARTICLES

Cathode Rays - Discovery of Electron

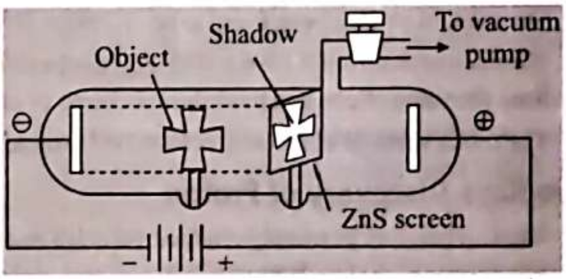

Cathode rays
Gas at low pressure
vacuum pump
Cathode
Anode
−
+
High voltage

(*a*) The electron was discovered as a result of the studies of the passage of electricity through gases at extremely low pressures known as Gas-discharge tube experiment.

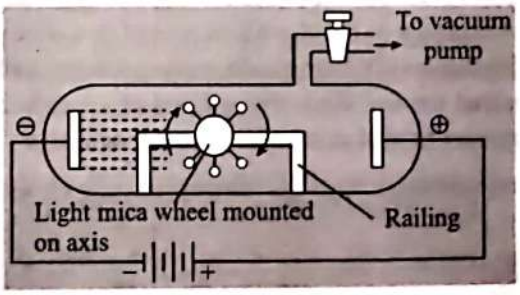
(*b*) When a high voltage of the order of 10,000 volts or more was applied across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrodes, these rays are called as cathode rays.

(*c*) Cathode rays have the following properties.

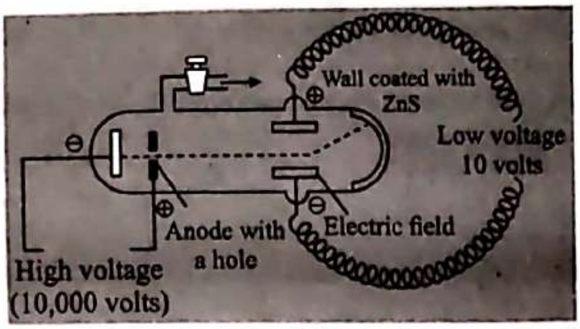
   (*i*) Path of travelling is straight from the cathode with a very high velocity, and it produces shadow of an object placed in its path.


Object
Shadow
To vacuum pump
⊖
⊕
ZnS screen
−
+

   (*ii*) Cathode rays produce mechanical effects. If a small pedal wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of matter.


To vacuum pump
⊖
⊕
Light mica wheel mounted on axis
Railing
−
+

   (*iii*) When electric and magnetic fields are applied to the cathode rays in the discharge tube, the rays are deflected thus establishing that they consist of charged particles.



(*iv*) Cathode rays produce X-rays when they strike against hard metals like tungsten, copper etc.

(*v*) When the cathode rays are allowed to strike on a thin metal foil, it gets heated up.

(*vi*) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.

(*vii*) Cathode rays penetrate through thin sheets of aluminium and other metals.

(*viii*) They affect the photographic plates.

(*ix*) **The ratio of charge to mass i.e. charge/mass is same for all the cathode rays irrespective of the gas used in the tube.**

Properties of Electron:

(*a*) The first precise measurement of the charge on an electron was made by Robert A. Millikan in 1909 by oil drop experiment. Its value was found to be -1.6022×10^{-19} coulomb.

(*b*) The value of e/m has been found to be -1.7588×10^{11} C/kg.

(*c*) The mass of electron (9.1096×10^{-31} Kg) can be calculated from the value of e/m and the value of charge of electron.

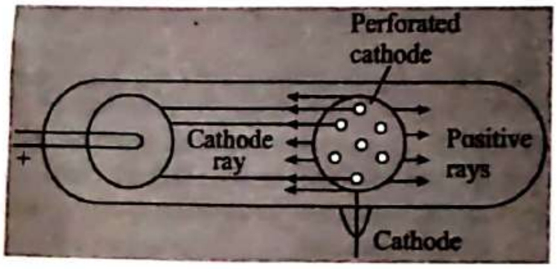
(*d*) The molar mass of electron is 5.48×10^{-4} g/mole.

Positive Rays-Discovery of Proton

(*a*) The existence of positively charged particles in an atom was shown by E. Goldstein in 1886.

(*b*) He repeated the Gas discharge tube experiments by using a perforated cathode.

(*c*) It was observed that when a high potential difference was applied between the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canal of the cathode. These rays are termed as canal rays or cathode rays.



(*d*) Characteristics of Anode Rays are as follows.

(*i*) These rays travel in straight lines and cast shadow of the object placed in their path.

(*ii*) The anode rays are deflected by the magnetic and electric fields like cathode rays but direction is opposite that mean these rays are positively charged.

(*iii*) These rays have kinetic energy and produces heating effect also.

(*iv*) The e/m ratio of these rays is smaller than that of electrons.

(*v*) **Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube.**

(*vi*) These rays produce flashes of light on ZnS screen.

(*vii*) These rays can pass through thin metal foils.

(*viii*) They are capable to produce ionisation in gases.

Properties of Proton

(*a*) Proton carries a charge of $+1.602 \times 10^{-19}$ coulomb, i.e., one unit positive charge.

(*b*) Mass of proton is 1.672×10^{-27} kg or 1.0072 amu.

(*c*) A proton is defined as a sub-atomic particle which has a mass nearly 1 amu and a relative charge of +1 unit.

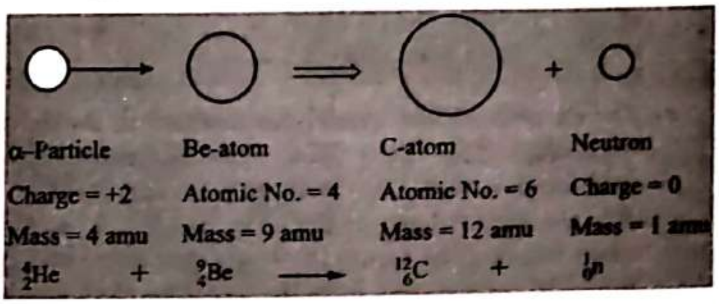
Discovery of Neutron

(*i*) This was discovered 20 years after the structure of atom was elucidated by Rutherford.

(*ii*) It has been found that for all atoms except hydrogen atomic mass is more than the atomic number. Thus Rutherford (1920) suggested that in an atom, there must be present at least a third type of fundamental particle.

(*iii*) It should be electrically neutral and posses mass nearly equal to that of proton. He proposed its name as neutron.

(*iv*) In 1932, **Chadwick** bombarded beryllium with a stream of α-particles. He observed that penetrating radiations were produced which were not affected by electric & magnetic fields. These radiations consists of neutral particles, which were called **neutrons**. The nuclear reaction can be shown as.



Properties of Neutron

(*a*) A neutron is a sub atomic particle which has a mass 1.675×10^{-24} g approximately 1amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.

(*b*) The specific charge (e/m value) of a **neutron** is zero.

Train Your Brain

Example 1: Which has highest e/m ratio?

(*a*) He^{2+} (*b*) H^+

(*c*) He^+ (*d*) H

Sol. (*b*) Mass of H^+ is minimum

Example 2: Arrange the following particles in increasing order of values of e/m ratio: Electron (*e*), proton (p), neutron (n) and α-particle (α):

(*a*) n, p, e, α (*b*) n, α, p, e

(*c*) n, p, α, e (*d*) e, p, n, α

Sol. (*b*)

	Electron	Proton	Neutron	α-particle
e	1 unit	1 unit	zero	2 units
m	1/1837 unit	1 unit	1 unit	4-units
e/m	1837	1	zero	1/2

Example 3: Mass of neutron is .... times the mass of electron:

(*a*) 1840 (*b*) 1480

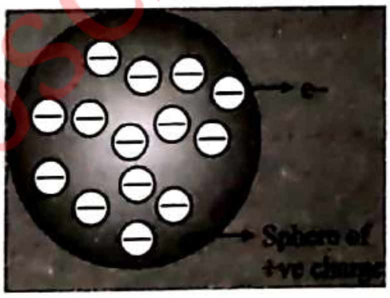
(*c*) 2000 (*d*) None of these

Sol. (*a*) Mass of neutron = 1.675×10^{-27} kg, mass of electron = 9.108×10^{-31} kg.

Concept Application

1. The mass of cathode ray particle is:
   (*a*) Same for different gases
   (*b*) Different for different gases
   (*c*) Minimum for H_2 gas
   (*d*) Different for same gases

THOMSON'S MODEL OF ATOM



Thomson was the first to propose a detailed model of the atom.

Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.

This model of atom is known as "Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".

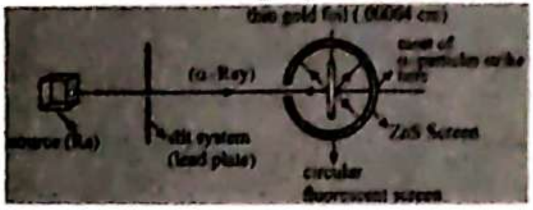
Drawbacks: An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.

It is a static model. It does not reflect the movement of electron.

It couldn't explain the stability of an atom.

RUTHERFORD'S SCATTERING EXPERIMENT

α-scattering experiment



Rutherford Observed that

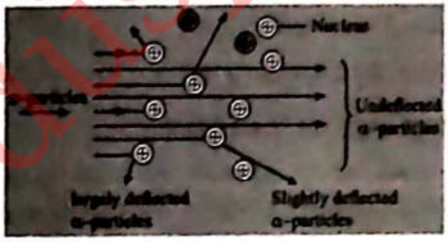
(*i*) Most of the α-particles (nearly 99.9%) went straight without suffering any deflection.

(*ii*) A few of them got deflected through small angles.

(*iii*) A very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in the direction from which they have come i.e. a deflection of 180°.

Following conclusions were drawn from the above observations:

(1) Since most of the α-particle went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.



(2) Since few of the α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.

When α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.

The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus.** It is supposed to be present at the centre of the atom.

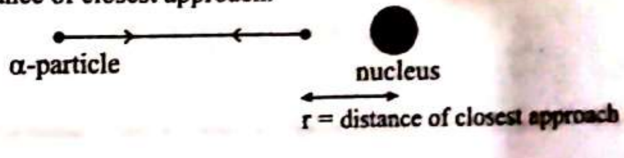
(3) A very few of the α-particles suffered strong deflections or even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

(4) Almost all mass of the atom is densely concentrated in extremely small region (nucleus).

(5) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Electrons and the nucleus are held together by electrostatic forces of attraction.

DISTANCE OF CLOSEST APPROACH

Rutherford estimated the size of nucleus by calculating the distance of closest approach.



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The initial kinetic energy of α-particle must be equal to potential energy at distance of closest approach.

$$\text{K.E.} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{q_1 . q_2}{r} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{(2e).(Ze)}{r}$$

$$\boxed{r = \frac{2Ze^2}{(4\pi\varepsilon_0)(\text{K.E.})}}$$

where Z = atomic number of element used in foil.

APPLICATIONS OF RUTHERFORD MODEL

On the basis of scattering experiments, Rutherford proposed model of the atom, which is known as nuclear atomic model. According to this model-

$$\frac{R_A}{R_N} = \frac{\text{Radius of the atom}}{\text{Radius of the nucleus}} = \frac{10^{-8}\text{ cm}}{10^{-13}\text{ cm}} = 10^5,$$

$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3}$ cm

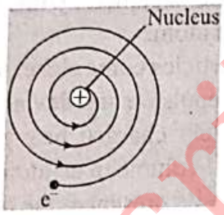
Where $R_0 = 1.33 \times 10^{-13}$ (a constant) and A = mass number (p + n) and R = radius of the nucleus.

$$\boxed{R = 1.33 \times 10^{-13}\ A^{1/3}\ \text{cm}}$$

$$\frac{\text{volume of the atom}}{\text{volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

Drawbacks of Rutherford Model

This theory could **not** explain stability of atom. According to Maxwell, electron loses its energy continuously in the form of electromagnetic radiations. As a result of this, the e^- should loss energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result is that it will fall into the nucleus, thereby making the atom unstable.



Train Your Brain

Example 4: An α-particles of kinetic energy of 10 MeV is projected towards gold nucleus. Calculate the distance of closest approach. (Atomic number of gold = 79, 1eV = 1.6×10^{-19} J)

Sol. $\text{K.E.} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{q_1 q_2}{r}$

or $10 \times 10^6 \times 1.6 \times 10^{-19} = 9 \times 10^9 \times \frac{(2\times1.6\times10^{-19})\times(79\times1.6\times10^{-19})}{r}$

$$\Rightarrow r = \frac{9\times10^9\times2\times1.6\times10^{-19}\times79}{10\times10^6} = 2.275\times10^{-14}\text{ m}$$

(From the above example it is clear that nuclear dimension cannot be greater than 3×10^{-14}m.)

Example 5: An α-particles is projected towards the following nucleus with same kinetic energy in different experiment the distance of closest approach is maximum for

(*a*) Na (Z = 11) (*b*) Ca (Z = 20)
(*c*) Ag (Z = 47) (*d*) Au (Z = 79)

Sol. (*d*) $K.E = \frac{kq_1q_2}{r}$

q_1 = charge of α-particle

q_1 = charge on nucleus of given element

therefore, $r = \frac{kq_1q_2}{K.E.}$

if K.E. = constant & $q_1 = 2e^-$

then $r \propto q_2$ i.e., atomic number of other element.

Concept Application

2. Rutherford's alpha particle scattering experiment eventually led to the conclusion that
   (*a*) Mass and energy are related
   (*b*) Electrons occupy space around the nucleus
   (*c*) Neutrons are buried deep in the nucleus
   (*d*) The point of impact with matter can be precisely determined

ATOMIC NUMBER (Z) AND MASS NUMBER (A)

Atomic number (Z) of an element

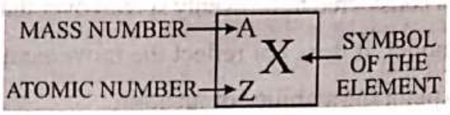
= Total number of protons present in the nucleus.

= Total number of electrons present in the neutral atom.

- Since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons.**
- As each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom (in amu).

Mass number of an element = No. of protons (Z) + No. of neutrons (n).

- The mass number of an element is nearly equal to the atomic mass of that element.
- The atomic number (Z) and mass number (A) of an element 'X' are usually represented along with the symbol of the element as



(i) **Isotopes:** Such atoms of the same element having same atomic number but different mass numbers are called isotopes.

e.g. $^1_1H, ^2_1D$ and ^3_1T and isotopes of hydrogen.

(ii) **Isobars:** Such atoms of different elements which have same mass numbers (and of course different atomic numbers) are called isobars.

e.g. $^{40}_{18}Ar, ^{40}_{19}K, ^{40}_{20}Ca$.

(iii) **Isotones:** Such atoms of different elements which contain the same number of neutrons are called isotones.

e.g. $^{14}_{6}C, ^{15}_{7}N, ^{16}_{8}O$.

(iv) **Isoelectronic species:** The species (atoms or ions) containing the same number of electrons are called isoelectronic species.

For example: O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, Ne all contain 10 electrons each and hence they are isoelectronic.

(v) **Isodiaphers:** Such atoms having same difference in the number of protons and neutrons in their nucleus i.e., same value of (n-p).

e.g. U^{238}_{92} and Th^{234}_{90}

NATURE OF LIGHT AND NATURE OF ELECTROMAGNETIC RADIATION

Nature of Light

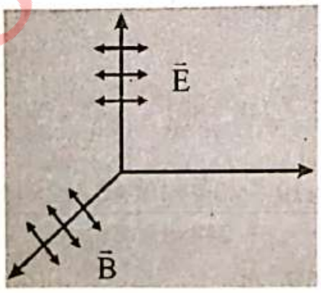
- **Maxwell electromagnetic wave theory (wave nature of light):** An accelerated electrically charged particle produces and transmits electrical and magnetic field. These are transmitted in the form of waves known as electromagnetic waves or electromagnetic radiations.

  He stated that light also possess electrical and magnetic field and it is also known as electromagnetic radiations.

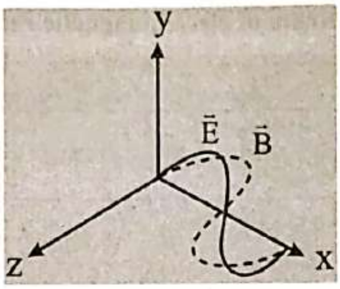
- **Characteristics of Electromagnetic Radiations:**
  - *(i)* In these electromagnetic radiation electrical and magnetic field oscillates perpendicular to each other and it also propagates perpendicular to both field.
  - *(ii)* All these electromagnetic radiation do not require any medium and can travel in vacuum.
  - *(iii)* Velocity of all electromagnetic radiations is 3×10^8 m/s in vacuum.
  - *(iv)* Energy of an electromagnetic wave is directly proportional to intensity and it is independent of frequency.
  - *(v)* They also show diffraction and interference and therefore, Maxwell concluded light to be wave nature.

Electromagnetic Wave Radiation

The form of energy which propagates in form of the oscillating electrical/magnetic field are called electromagnetic radiations.

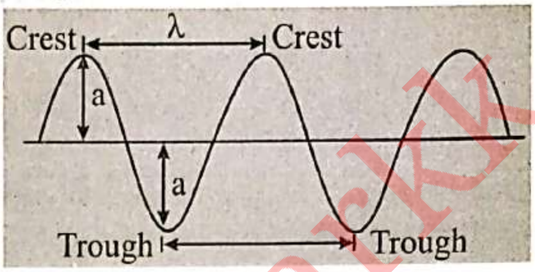


$\vec{E}$ = Electric field, $\vec{B}$ = Magnetic field



Direction of wave propagation.

Some important characteristics of a wave:



(i) **Wavelength** of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (Lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$

$1 \text{ nm} = 10^{-9} \text{ m}, 1 \text{ pm} = 10^{-12} \text{ m}$

(ii) **Frequency** of a wave is defined as the number of waves passing through a point in one second. It is represented by ν (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec^{-1} or s^{-1}.

1 Hz = 1 cycle/sec

(iii) **Velocity** of a wave is defined as the linear distance travelled by the wave in one second. It is represented by v and is expressed in cm/sec or m/sec (ms^{-1}).

(iv) **Amplitude** of a wave is the height of the crest or the depth of the trough. It is represented by 'A' and is expressed in the units of length.

(v) **Wave number** is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by $\bar{\nu}$ (read as nu bar).

$$\bar{\nu} = \frac{1}{\lambda}$$

If λ (Lambda) is expressed in cm, $\bar{\nu}$ will have the units cm^{-1}.

Relationship between velocity, wavelength and frequency of a wave: As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave.

Wave speed = Frequency × Wavelength

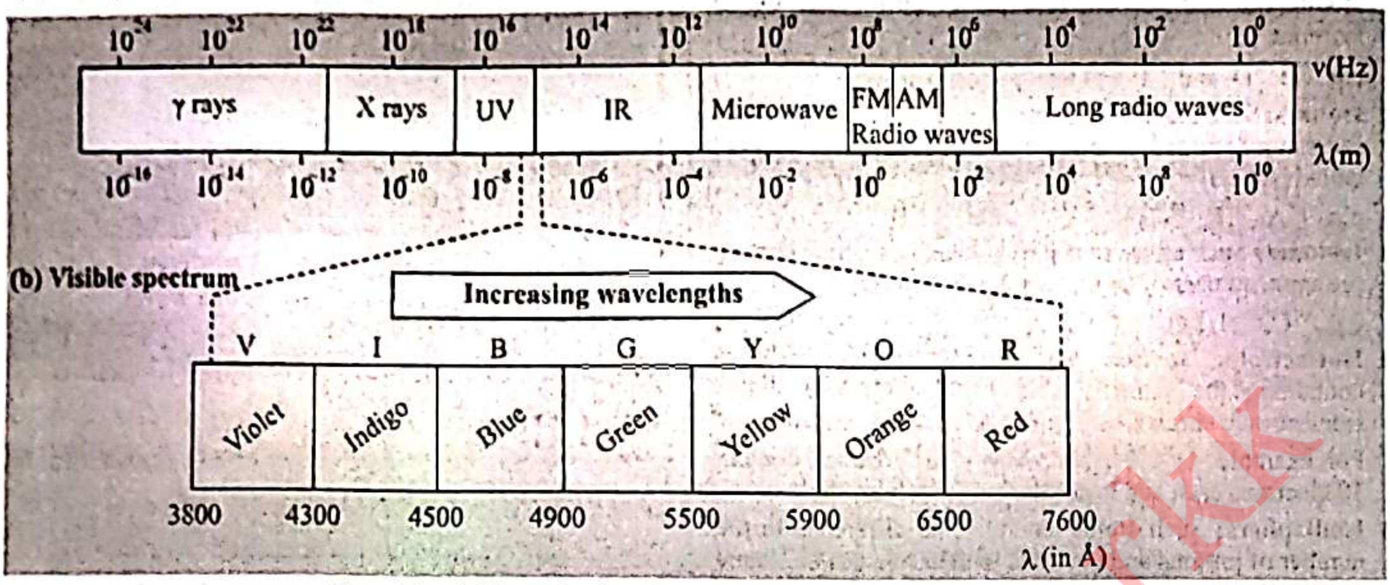
ELECTRO MAGNETIC SPECTRUM

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequencies is known as electromagnetic spectrum.

Order of wavelength in Electromagnetic spectrum:

Cosmic rays < γ-rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

(a) The spectrum of electromagnetic radiation.


10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0}
ν(Hz)
γ rays
X rays
UV
IR
Microwave
FM AM
Radio waves
Long radio waves
λ(m)
10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0} 10^{2} 10^{4} 10^{8} 10^{10}
(b) Visible spectrum
Increasing wavelengths
V I B G Y O R
Violet
Indigo
Blue
Green
Yellow
Orange
Red
3800 4300 4500 4900 5500 5900 6500 7600
λ (in Å)

Note: The visible region is only a small part of the entire spectrum.

PLANCK'S QUANTUM THEORY

Particle nature of light: He stated that a body radiates energy in the form of discontinuous energy packets or bundles. Each bundle of energy is known as quantum and quantum of light is known as photons.

Energy of each quantum is directly proportional to frequency of radiation.

$$E \propto \nu$$

$$E = h\nu \qquad \underset{\substack{\downarrow \\ \text{Planck's constant}}}{h = 6.62 \times 10^{-34}\ \text{J-s}}$$

Total energy absorbed or emitted by a body will be whole no. integral multiple of energy of quantum.

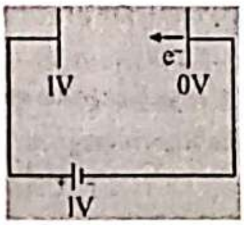
$$E = \frac{nhc}{\lambda}$$

Key Note

1. **One electron volt (e.v.):** Energy gained by an electron when it is accelerated from rest through a potential difference of 1 volt.
2. Positive charge always moves from high potential to low potential and –ve charge always moves from low potential to high potential if set free.
3. If a charge 'q' is accelerated through a potential difference of 'V' volt then its kinetic energy will be increased by q × V.

   $1\text{eV} = 1.6 \times 10^{-19}\ \text{C} \times 1\ \text{volt}$

   $\therefore 1\text{eV} = 1.6 \times 10^{-19}\text{J}$



Train Your Brain

Example 6: Calculate the no. of photons emitted by 60 watt bulb in 10 hrs, when light of wavelength 6000 Å is emitted by it.

Sol. $P = \frac{E}{t} = \frac{nh\upsilon}{t}$ or $P = \frac{nhc}{\lambda t}$ or $n = \frac{P \times \lambda \times t}{h \times c}$

or $n = \dfrac{60 \times 6000 \times 10^{-10} \times 10 \times 60 \times 60}{6.626 \times 10^{-34} \times 3 \times 10^{8}}$

or $n = 6.52 \times 10^{24}$

Example 7: Certain sun glasses have small amount of AgCl incorporated in the lenses which on exposure to light of appropriate wavelength turns to gray colour to reduce the glare following the reactions:

$$AgCl \xrightarrow{h\nu} Ag(Gray) + Cl$$

If the heat of reaction for the decomposition of AgCl is 248 kJ mol^{-1}, what maximum wavelength is needed to induce the desired process?

Sol. Energy needed to change = 248×10^3 J/mol

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon. Therefore,

$$\therefore\ N_A \cdot \frac{hc}{\lambda} = 248 \times 10^3$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^{8} \times 6.022 \times 10^{23}}{248 \times 10^{3}}$$

$$= 4.83 \times 10^{-7}\ \text{m}$$

Example 8: A bulb is rated as 110 watt. If it emits 25% of absorbed energy as red light ($\lambda = 6626Å$), how many photons are emitted out by the bulb per second?

Sol. $P \times \eta = \frac{n \times h \times c}{\lambda \times t}$

or $110 \times \frac{25}{100} = n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{6626 \times 10^{-10}}$

or $n = 9.2 \times 10^{19}$

Example 9: Wavelength of micro wave radiation is 0.08 m. How many moles of photons is needed to increase the temperature of 400 gm water from 25° to 45°C, assuming 25% efficiency?

Specific heat capacity = 4.2 J/K.gm

Sol. $\left(\frac{nhc}{\lambda}\right) \times \frac{25}{100} = ms\Delta t$

$$n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{0.08} \times \frac{25}{100} = 400 \times 4.2 \times 20$$

$\therefore$ Number of moles of photon $= \frac{n}{N_A}$

or Number of moles of photon $= \frac{540.89 \times 10^{26}}{6.022 \times 10^{23}}$

$= 9.0 \times 10^{4}$ mol.

Example 10: A dye absorbs the radiation of 4000 Å and fluoresces the radiation of 5000 Å. If only 40% of the absorbed energy is emitted out, calculate the ratio of number of quanta emitted out and the number of quanta absorbed.

Sol. $E_a \times \frac{40}{100} = E_e$

$$n_a \times \frac{hc}{4000Å} \times \frac{40}{100} = n_e \times \frac{hc}{5000Å}$$

$$\frac{n_e}{n_a} = \frac{40}{100} \times \frac{5000}{4000} = \frac{1}{2} \Rightarrow \frac{n_e}{n_a} = \frac{1}{2}$$

Concept Application

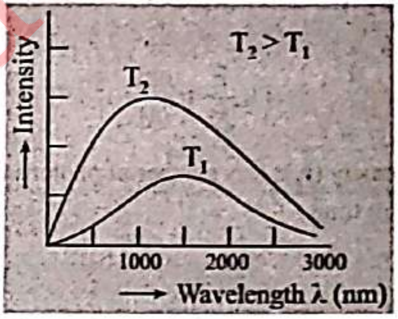
3. Photon of which light has maximum energy:
   (a) Red (b) Blue
   (c) Violet (d) Green
4. Two bulbs 'A' and 'B' emit red light and yellow light at 8000 Å and 4000Å respectively. The number of photons emitted by both the bulbs per second is the same. If the red bulb is labelled as 100 watts, find the wattage of the yellow bulb.
   (a) 100 watt (b) 200 watt
   (c) 300 watt (d) 400 watt
5. The Vividh Bharati Station of All India Radio, Delhi broadcasts on a frequency of 1368 kHz (kilo hertz). Calculate the wavelength and wave number of the electromagnetic radiation emitted by the transmitter.
   (a) (219.3 m, 4.56×10^{-3} m^{-1})
   (b) (219.2 m, 4.46×10^{-3} m^{-1})
   (c) (218.3 m, 4.56×10^{-3} m^{-1})
   (d) (219.5 m, 4.58×10^{-3} m^{-1})

APPLICATION OF PLANCK'S QUANTUM THEORY

Black Body Radiation:

When solids are heated they emit radiation over a wide range of wavelengths.

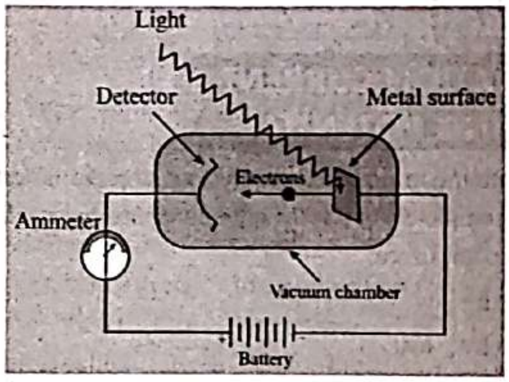
The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature.



The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities.

Photoelectric Effect:

When certain metals (for example: Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected as shown in Fig.



The phenomenon is called **Photoelectric effect.** The results observed in this experiment were:

- The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
- The number of electrons ejected is proportional to the intensity or brightness of light.

TERMS USED IN PHOTO ELECTRIC EFFECT

1. **Work function (w):** It is the minimum amount of energy required to cause a photo emission from the metal surface. It is also known as threshold energy or Binding energy. Work function depends upon ionisation energy and therefore w is minimum for alkali metals.
2. **Threshold frequency (ν_0):** The minimum value of frequency that can cause photo emissions. If $\nu < \nu_0$, then there is no photo emission.

$$w = h\nu_0 \Rightarrow w = \frac{hc}{\lambda_0}$$

3. **Threshold wavelength (λ_0):** The maximum value of wavelength that can cause photo emission.

   If $\lambda > \lambda_0$, then photo emission is not possible.
4. **Intensity (I):** Energy falling on metal surface of unit area per unit time.

$$I = \frac{E}{At} = \frac{nh\nu}{At}$$

5. **Photo intensity (I_P):** It is number of photons falling per unit area per unit time.

$$I_P = \frac{n}{At}$$

Relation between I and I_p:

$I = I_p h\nu$

Photo intensity is independent of frequency while intensity depends on frequency.

Power: Total energy radiated per unit time.

$$P = \frac{E}{t} = \frac{nh\nu}{t}$$

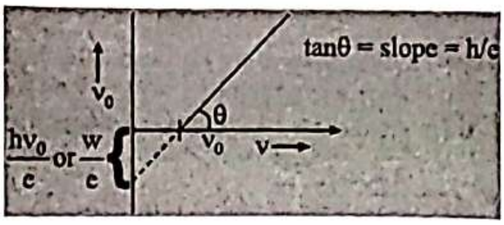
SATURATION CURRENT & STOPPING POTENTIAL

It is the minimum potential required to stop the fastest moving electrons completely or it is the minimum potential at which photo current becomes zero.

$eV_0 = h\nu - w$

$eV_0 = h\nu - h\nu_0$

$$\Rightarrow V_0 = \frac{h\nu}{e} - \frac{h\nu_0}{e}$$



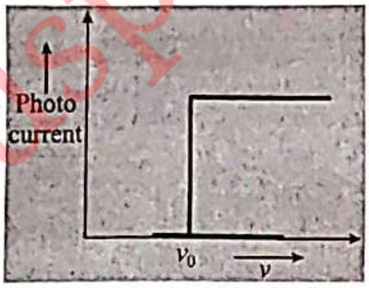
It can be commented that stopping potential increase with increase in frequency. However, if photo intensity is changed there is no effect on stopping potential.

On increasing the intensity of light the stopping potential does not change because the maximum K.E. of photoelectron does not change, but the photocurrent increases, because the number of photon falling on the surface increases.

EFFECT OF VARIATION OF FREQUENCY

(*a*) **Effect on Photo Emission:** $I = I_p h\nu$

If frequency of subjected photon increases (intensity increases keeping photo intensity constant) then there is no change in no. of ejected photo electrons as well as no change in photo current.



(*b*) **Effect on kinetic Energy:** Average K. E. as well as K. E_{max} increases with increases in frequency.

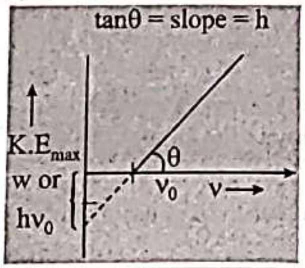
$h\nu - W = KE_{max}$.

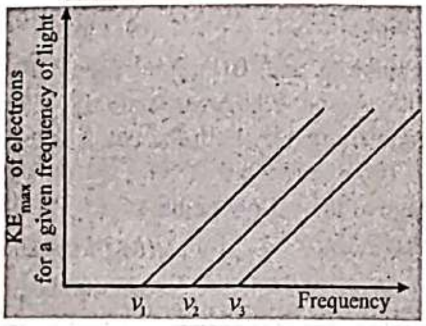
$KE_{max} = h\nu - h\nu_0$

$y = mx + c$

$$KE_{max} = h\nu - \frac{hc}{\lambda_0}$$

$KE_{max} = h\nu - w$

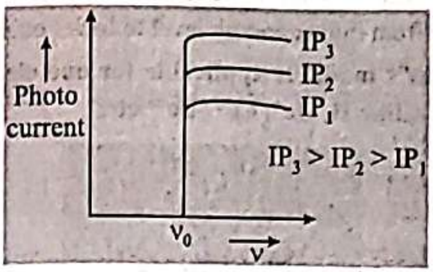




The diagram shows the interdependence between light frequency and the K.E.$_{max}$ of electrons emitted from metal. It shows the interdependence for three different metals. See that it clearly shows the limiting frequencies are different for different metals.

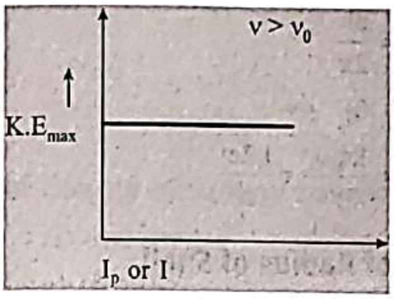
Effect of Variation of Photo Intensity

On increasing intensity, keeping frequency constant (i.e. increasing photo intensity) no. of ejected photo electrons increases as well as photo current increases.



Effect on Kinetic Energy

Average K.E. and K.E$_{max}$ remains constant with change in photo intensity



Train Your Brain

Example 11: Ultraviolet light of wavelength 200 nm is used in an experiment of photoelectric effect with lithium cathode (w = 2.5 eV). Then calculate

(*i*) K.E$_{max}$ (*ii*) Stopping potential

Sol. $K.E._{max} = \frac{hc}{\lambda} - w$

$$K.E._{max} = \frac{6.626\times10^{-34}\times3\times10^{8}}{200\times10^{-9}\times1.6\times10^{-19}} - 2.5\ eV$$

= 6.2 – 2.5 = 3.7 eV

Stopping Potential = 3.7 V

Example 12: A photon of wavelength 3000 Å strikes a metal surface, the work function of the metal being 2.20 eV. Calculate (*i*) the energy of the photon in eV (*ii*) the kinetic energy of the emitted photo electron and (*iii*) the velocity of the photo electron.

Sol. (*i*) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6\times10^{-34}\,Js)(3\times10^{8}\,ms^{-1})}{3\times10^{-7}\,m} = 6.6\times10^{-19}\,J$$

$1\ eV = 1.6\times10^{-19}\,J$

$$\text{Therefore } E = \frac{6.6\times10^{-19}\,J}{1.6\times10^{-19}\,J/eV} = 4.125\ eV$$

(*ii*) Kinetic energy of the emitted photo electron

Work function = 2.20 eV

Therefore, K.E. = 4.125 – 2.20

= 1.925 eV = 3.08 × 10^{-19} J

(*iii*) Velocity of the photo electron

$$K.E. = \frac{1}{2}mv^2 = 3.08\times10^{-19}\,J$$

Therefore,

$$\text{velocity }(v) = \sqrt{\frac{2\times3.08\times10^{-19}}{9.1\times10^{-31}}} = 8.22\times10^{5}\,ms^{-1}$$

Example 13: The threshold frequency ν_0 for a metal is 6 × 10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency ν = 1.1 × 10^{15} s^{-1} hits the metal.

Sol. $K.E. = \frac{1}{2}m_e v^2 = h(\nu - \nu_0)$

∴ K.E. = (6.626 × 10^{-34}) (1.1 × 10^{15} – 6 × 10^{14})

= 3.3 × 10^{-19} J

Concept Application

6. A photon of energy hν is absorbed by a free electron of a metal having work function w < hν. Then:
   (*a*) The electron is sure to come out
   (*b*) The electron is sure to come out with a kinetic energy (hν – w)
   (*c*) Either the electron does not come out or it comes with a kinetic energy (hν – w)
   (*d*) It may come out with a kinetic energy less than (hν – w)

7. A beam of white light is dispersed into its wavelength components by a Quartz prism and falls on a thin sheet of potassium metal. What is the correct decreasing order of kinetic energy of the electron emitted by the different light component?
   (*a*) blue > green > orange > yellow
   (*b*) violet > blue > orange > red
   (*c*) yellow > green > blue > violet
   (*d*) orange > yellow > blue > violet

8. A laser producing monochromatic lights of different wavelength is used to eject electron from the sheet of gold having threshold frequency $6.15 \times 10^{14}\ s^{-1}$. Which of the following incident radiation will be suitable for the ejection of electrons?

(*a*) 1.5 moles of photons having frequency $3.05 \times 10^{14}\ s^{-1}$

(*b*) 0.5 moles of photon of frequency $12.3 \times 10^{12}\ s^{-1}$

(*c*) One photon with frequency $5.16 \times 10^{15}\ s^{-1}$

(*d*) All of the above

9. The number of photoelectrons emitted depends upon:

(*a*) The intensity of the incident radiation

(*b*) The frequency of the incident radiation

(*c*) The product of intensity and frequency of incident radiation

(*d*) None of these

BOHR'S MODEL

It was the first model based on Planck's quantum theory and the model explained stability of atom and line spectrum of hydrogen.

Postulates of Bohr's Model

(*i*) An atom consist of centrally located small, dense, positively charged nucleus and electrons are revolving around the nucleus in circular paths known as circular orbits and coulombic force of attraction between nucleus and electron is balanced by centrifugal force of the revolving electron.

(*ii*) Out of the infinite circular orbits only those circular orbits are possible in which angular momentum of electron is integral multiple of h/2π i.e. angular momentum of an electron can have fixed values like $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ etc. i.e., angular momentum of electron is quantised.

$$mvr = \frac{nh}{2\pi}$$

m and v are mass and velocities of electron respectively. r is radius of orbit and n is integer which is later related with orbit number or shell number and h is Planck's constant.

(*iii*) The energy of these circular orbits have fixed values and hence electron in an atom can have only certain values of energy. It is characteristic of an orbit and it cannot have any orbit value of its own. And therefore energy of an electron is also quantised.

(*iv*) As long as electrons remains in these fixed orbits, it doesn't loose energy i.e., energy of an electron is stationary (not changing with time) and therefore these orbits are known as allowed energy levels or stationary states and this explains the stability of atom.

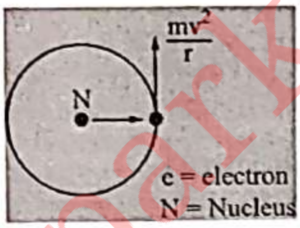
(*v*) The energy levels are designated as K, L, M, N and numbered as 1, 2, 3, 4 etc from nucleus outwards and as the distance of the shells or energy level from the nucleus increases the energy of the energy level also increases i.e., $E_N > E_M > E_L > E_K$

(*vi*) The emission or absorption of energy in the form of radiations can only occur when an electron jump from one stationary orbit to other.

$$\Delta E = E_{higher} - E_{lower}$$

ΔE = hν, where hν is the energy of absorbed photon or emitted photon which corresponds to the difference in energy levels. Energy is absorbed when electron jumps from lower energy level (normal state) to higher energy level (excited state) and energy is emitted when electrons jumps from higher energy level to lower energy level.

❖ **Bohr's model is applicable for one electron species only, like H, He^+, Li^{+2}, Be^{+3} etc.**



$$mvr = \frac{nh}{2\pi} \quad \ldots (i)$$

$$q_1 = e,\ q_2 = Ze$$

$$\frac{mv^2}{r} = \frac{kq_1q_2}{r^2} = \frac{kZe^2}{r^2} \quad \ldots (ii)$$

Derivation of Radius of Shell

$$\Rightarrow \frac{mn^2h^2}{4\pi^2m^2r^2 \cdot r} = \frac{kZe^2}{r^2}$$

$$\Rightarrow r = \frac{mn^2h^2}{4\pi^2m^2kZe^2} \Rightarrow \boxed{r = \frac{n^2h^2}{4\pi^2mkZe^2}}$$

$$r = 0.529 \times \frac{n^2}{z}\text{Å} \Rightarrow r \propto \frac{n^2}{z}$$

For a particular atom $r \propto n^2$

Radius of 1st orbit of H atom

r = 0.529 Å

Derivation of Velocity of Electron in Bohr's Orbit

$$v = \frac{nh}{2\pi mr}, \text{ putting value of r.}$$

$$v = \frac{nh \times 4\pi^2mkZe^2}{2\pi mn^2h^2}$$

$$v = \frac{2\pi kZe^2}{h.n} = \frac{2\pi ke^2}{h} \times \frac{Z}{n}$$

$$\boxed{v = 2.18 \times 10^6\ \frac{Z}{n}\ \text{m/s}}$$

$$v \propto \frac{Z}{n}$$

Derivation of Total Energy of Electron/System

T.E. of system = K.E. of e^- + P.E. of system (nucleus and e^-)

Kinetic energy of electron $= \frac{1}{2}mv^2 = \frac{1}{2}\frac{kZe^2}{r}$

$$P.E. = -\frac{kZe^2}{r}$$

$$T.E = \frac{-kZe^2}{2r} \qquad \left[r = \frac{n^2h^2}{4\pi^2m^2kZe^2}\right]$$

$$T.E. = -13.6 \times \frac{Z^2}{n^2}\ \text{eV/atom} \quad \text{...(i)}$$

$$T.E. = -2.18 \times 10^{-18}\ \frac{Z^2}{n^2}\ \text{J/atom}$$

As shell no. or distance increases, the value of T.E. and P.E. increases (however magnitude decreases) and becomes maximum at infinity i.e., zero.

$$K.E. = -\frac{P.E.}{2}$$

$$T.E. = \frac{P.E.}{2}$$

$$T.E. = -K.E.$$

Calculation of Energy of Energy Levels in H atom

(*i*) When n = 1 (ground level)

K.E. = 13.6 eV (atom)

P.E. = –27.2 eV / atom

T.E. = –13.6 eV/atom

(*ii*) When n = 2/2nd energy level / 1st excited state

$$K.E. = \frac{13.6}{4}\ \text{eV/atom} = 3.4\ \text{eV/ atom}$$

P.E. = – 6.8 eV/atom

T.E. = – 3.4 eV/atom

$E_2 - E_1 = -3.4 + 13.6$ eV/atom = 10.2 eV/atom

(*iii*) When n = 3 / 3rd energy level/2nd excited state.

$$K.E. = \frac{13.6}{9}\ \text{eV/atom} = 1.51\ \text{eV/atom}$$

P.E. = –3.02 eV/atom

T.E. = –1.51 eV/atom

$E_3 - E_2 = -1.51$ eV/atom + 3.4 eV/atom

= 1.89 eV atom.

(*iv*) When n = 4 / 3rd excited state

$$K.E. = \frac{13.6}{4^2} \Rightarrow \frac{13.6}{16} = 0.85\ \text{eV/atom}$$

P.E. = –1.70 eV/atom

T.E. = –0.85 eV/atom

$E_4 - E_3 = 0.66$

As distance increases (n increases) energy of the energy level increases but energy difference between consecutive energy level keeps on decreasing i.e., maximum energy difference is between 2 to 1 (among consecutive orbits).

Conclusion from Equation of Energy

(*a*) The negative sign of energy indicates that there is attraction between the negatively charged electron and positively charged nucleus.

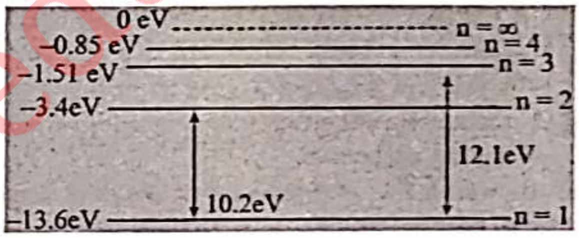
(*b*) All the quantities on R.H.S. in the energy equation are constant for an element having atomic number Z except 'n' which is an integer such as 1,2,3, etc. i.e. the energy of an electron is constant as long as the value of 'n' is kept constant.

(*c*) The energy of an electron is inversely proportional to the square of 'n' with negative sign.

Energy Level Diagram

(*i*) Orbit of lowest energy is placed at the bottom, and all other orbits are placed above this.

(*ii*) The gap between two orbits is proportional to the energy difference of the orbits.



Definitions Valid for Single Electron System

(*i*) **Ground State:** Lowest energy state of any atom or ion is called ground state of the atom, it is n = 1.

Ground state energy of H–atom = – 13.6 eV

Ground state energy of He^+ ion = – 54.4 eV

(*ii*) **Excited State:** States of atom other than the ground state are called excited states:

n = 2	First excited state
n = 3	Second excited state
n = 4	Third excited state
n = (n + 1)	nth excited state

(*iii*) **Ionisation Energy (I.E.):** Minimum energy required to move an electron from ground state to n = ∞ is called ionisation energy of the atom or ion.

Ionisation energy of H–atom = 13.6 eV

Ionisation energy of He^+ ion = 54.4 eV

Ionisation energy of Li^{+2} ion = 122.4 eV

(*iv*) **Ionisation Potential (I.P.):** Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom.

I.P. of H atom = 13.6 eV, I.P. of He^+ ion = 54.4 eV

(v) Excitation Energy: Energy required to move an electron from ground state of the atom to any other state of the atom is called excitation energy of that state.

Excitation energy of 2nd state = Excitation energy of 1st excited state = 1st excitation energy = 10.2 eV.

(vi) Excitation Potential: Potential difference through which an electron must be accelerated from rest to higher energy level, so that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.

e.g. in H-atom excitation potential of third state = excitation potential of second excited state = second excitation potential = 12.1 eV.

(vii) Binding Energy 'or' Separation Energy: Energy required to move an electron from any state to $n = \infty$ is called binding energy of that state.

Binding energy of ground state = I.E. of atom or ion.

Failures/Limitations of Bohr's theory

(a) He could not explain the line spectra of atoms containing more than one electron.

(b) He also could not explain the presence of multiple spectral lines.

(c) He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect).

(d) No conclusion was given for the principle of quantisation of angular momentum.

(e) He was unable to explain the de-Broglie's concept of dual nature of matter.

(f) He could not explain Heisenberg's uncertainty principle.

Train Your Brain

Example 14: A single electron system has ionization energy 11180 kJ mol^{-1}. Find the number of protons in the nucleus of the system.

Sol. $\text{I.E.} = \frac{Z^2}{n^2} \times 21.8 \times 10^{-19}$ J/atom

$$\frac{11180\times10^3}{6.022\times10^{23}} = \frac{Z^2}{1^2} \times 21.8 \times 10^{-19}$$

or $Z = 3$

Example 15: What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom?

Sol. Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series.

$$\Delta E = 2.18 \times 10^{-18}\text{ J}\left[\frac{1}{5^2}-\frac{1}{2^2}\right] = -4.58 \times 10^{-19}\text{ J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58\times10^{-19}\text{ J}}{6.626\times10^{-34}\text{ Js}} = 6.91 \times 10^{14}\text{ Hz and}$$

$$c = \nu\lambda \text{ or } \lambda = \frac{3\times10^8}{6.91\times10^{14}} \text{ or } \lambda = 434\text{ nm}$$

Example 16: The ionization energy of He$^+$ is 19.6×10^{-18} J atom^{-1}. The energy of the first stationary state of Li^{+2} will be

(a) 21.2×10^{-18} J/atom (b) 44.10×10^{-18} J/atom

(c) 63.2×10^{-18} J/atom (d) 84.2×10^{-18} J/atom

Sol. (b) E_1 for Li^{+2} = E_1 for H × $Z^2{}_{Li}$ = E_1 for H × 9

E_1 for He$^+$ = E_1 for H × $Z^2{}_{He}$ = E_1 for H × 4

or E_1 for Li^{+2} = $\frac{9}{4}$ E_1 for He$^+$

$$= 19.6 \times 10^{-18} \times \frac{9}{4}$$

$$= 44.10 \times 10^{-18}\text{ J/atom}$$

Example 17: Calculate ratio of radius of 2nd orbit of H atom to 3rd orbit of Li^{+2} ion.

Sol. $$\frac{\text{Radius of 2}^{\text{nd}}\text{ orbit of H atom}}{\text{Radius of 3}^{\text{rd}}\text{ orbit of Li}^{+2}\text{ atom}}$$

$$= \frac{n^2}{z}\times\frac{z_1}{n_1^2} = \frac{4}{3}$$

Concept Application

10. Consider Bohr's theory for hydrogen atom. The magnitude of angular momentum, orbit radius and velocity of the electron in nth energy state in a hydrogen atom are l, r & v respectively. Find out the value of 'x', if product of v, r and l (vrl) is directly proportional to n^x.

(a) (x = 1) (b) (x = 2)

(c) (x = 3) (d) (x = 4)

11. Correct order of radius of the Ist orbit of H, He$^+$, Li^{2+}, Be^{3+} is:

(a) H > He$^+$ > Li^{2+} > Be^{3+}

(b) Be^{3+} > Li^{2+} > He$^+$ > H

(c) He$^+$ > Be^{3+} > Li^{2+} > H

(d) He$^+$ > H > Li^{2+} > Be^{3+}

12. A single electron ion has nuclear charge + Ze where Z is atomic number and e is electronic charge. It requires 16.52 eV to excite the electron from the second Bohr orbit to third Bohr orbit. Then atomic number and kinetic enrgy of electron in first Bohr orbit are respectively:

(*a*) Z = 3, K.E. = 122.4 eV

(*b*) Z = 3, K.E. = 122.2 eV

(*c*) Z = 2, K.E. = 122.4 eV

(*d*) Z = 3, K.E. = 121.4 eV

13. Match the following

A.	Energy of ground state of He^+	(i)	+ 6.04 eV
B.	Potential energy of I orbit of H-atom	(ii)	–27.2 eV
C.	Kinetic energy of II excited state of He^+	(iii)	54.4 V
D.	Ionisation potential of He^+	(iv)	– 54.4 eV

(*a*) A – (i), B – (ii), C – (iii), D – (iv)

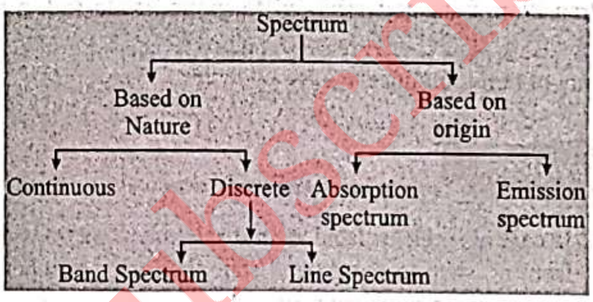
(*b*) A – (iv), B – (iii), C – (ii), D – (i)

(*c*) A – (iv), B – (ii), C – (i), D – (iii)

(*d*) A – (ii), B – (iii), C – (i), D – (iv)

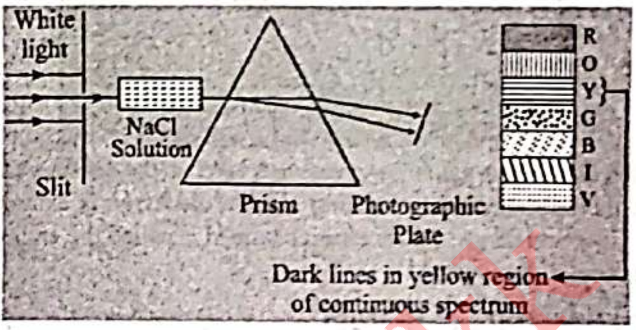
SPECTRUM

Study of Emission and Absorption Spectra: An instrument used to separate the radiation of different wavelengths (or frequencies) is called spectroscope or a spectrograph. Photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation The branch or science dealing with the study of spectra is called **spectroscopy.**


Spectrum
Based on Nature
Based on origin
Continuous
Discrete
Absorption spectrum
Emission spectrum
Band Spectrum
Line Spectrum

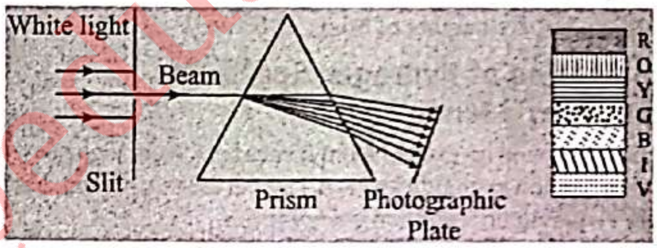
Emission spectra: When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc., is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'.

Absorption spectra: When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the continuous spectrum. These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations of certain wavelengths are absorbed, depending upon the nature of the element.


White light
NaCl Solution
Slit
Prism
Photographic Plate
R
O
Y
G
B
I
V
Dark lines in yellow region of continuous spectrum

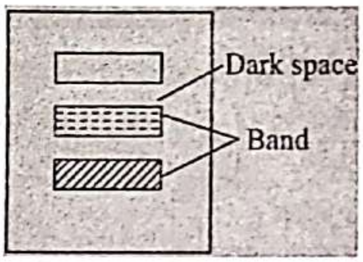
Depending upon the source of radiation, the emission spectra are mainly of two type:

Continuous Spectra: When white light from any source such as sun, a bulb or any hot glowing body is analysed by passing through a prism it is observed that it splits up into seven different wide band of colours from violet to red. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.


White light
Beam
Slit
Prism
Photographic Plate
R
O
Y
G
B
I
V

Discontinuous Spectrum: It is of two type:

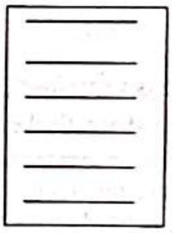
(*i*) **Band spectrum**


Dark space
Band

Band spectrum contains colourful continuous bands separated by some dark space.

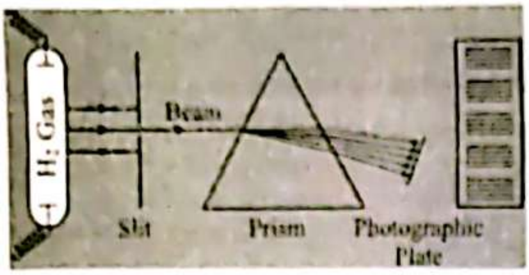
Generally molecular spectrum are band spectrum.

(*ii*) **Line Spectrum:**



This is the ordered arrangement of lines of particular wavelength separated by dark space e.g. hydrogen spectrum. Line spectrum can be obtained from atoms.

Emission Spectrum of Hydrogen



When dihydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

Line Spectrum of H-atom

The spectrum of H-atom is observed as discontinue line spectra. The different lines observed in H-spectrum were classified into different series and named after their discoverers.

Rydberg gave an empirical formula to calculate wavelength, which is applicable to all series.

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$R_H = 109677\ cm^{-1}$ Rydberg's constant.

n_1 and n_2 are number of orbits involved.

Explanation of Hydrogen Spectrum using Bohr's Model

When electron in an excited atom comes back from higher energy level (n_2) to lower energy level (n_1) then it emits a photon, having energy equal to difference in energy levels.

$$h\nu = \Delta E = E_{n_2} - E_{n_1}$$

$$h\nu = \frac{-2\pi^2 mk^2e^4z^2}{n_2^2h^2} - \left(-\frac{2\pi^2 mk^2e^4z^2}{n_1^2h^2}\right)$$

$$h\nu = \frac{2\pi mk^2e^4z^2}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \frac{2\pi mk^2e^4z^2}{h^3c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

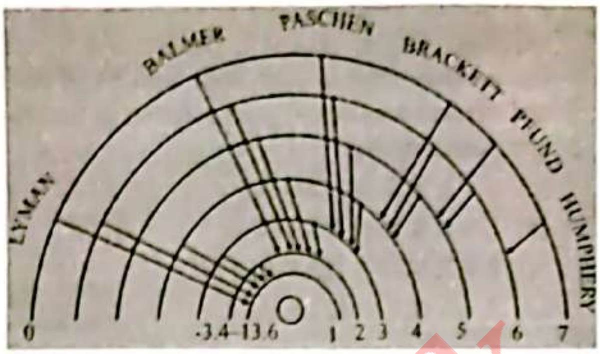
The theoretical value is very close to observed value.

∴ Bohr's model provides theoretical explanation of H-spectrum.

Wavelength or wave no. of any line of any one electron species can be calculated as:

$$\frac{1}{\lambda} = R_H Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right], \qquad \frac{hc}{\lambda} = \Delta E$$

Different Series in Hydrogen Spectrum



Series	Discovered by	Regions	n_2	n_1
Lyman	Lyman	U.V. region	$n_2 = 2,3,4...$	$n_1=1$
Balmer	Balmer	Visible region	$n_2 = 3,4,5...$	$n_1=2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4,5,6...$	$n_1=3$
Brackett	Brackett	I.R. region	$n_2 = 5,6,7...$	$n_1=4$
Pfund	Pfund	I.R. region	$n_2 = 6,7,8...$	$n_1=5$
Humphery	Humphery	Far I.R. region	$n_2 = 7,8,9...$	$n_1=6$

Key Points

First line / Starting line / Initial line (λ_{max} and ν_{min})

Last line / limiting line / Series limit (λ_{min} and ν_{max})

First line of any series = α line

Second line of any series = β line

Third line of any series = γ line

Total no. of emission lines between n_2 & n_1 = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

For transition from any orbit 'n' to ground state (i.e. n = 1), total no. of emission lines = $\frac{n(n-1)}{2}$

Key Note

- In case of single isolated atom if electron make transition from n^{th} state to the ground state then max. number of spectral lines observed = (n – 1).

SPECTRA LINES OF HYDROGEN ATOM

Lyman Series

- It is first spectral series of H-atom.
- It was found out in ultraviolet region in 1898 by Lyman.
- It has $n_1 = 1$ and $n_2 = 2,3,4$ where 'n_1' is ground state and 'n_2' is called excited state of electron present in a H - atom.

- $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 1$ always.
- The wavelength of marginal line $= \frac{n_1^2}{R_H}$ for all series. So for Lyman series $\lambda = \frac{1}{R_H}$.
- I^{st} line of lyman series = 2 → 1
- II^{nd} line of lyman series = 3 → 1
- Last line of lyman series = ∞ → 1
- First line of any spectral series is the longest (λ_{max}) line.
- Last line of any spectral series is the shortest (λ_{min}) line.

Series limit: It is the last line of any spectral series.

Wave no. of I^{st} line of Lyman series

$$= \frac{1}{\lambda} = \bar{\nu} = R_H \times 1^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$\bar{\nu} = R_H \times 1^2\left(\frac{4-1}{4}\right)$$

$$\bar{\nu} = \frac{R_H \times 3}{4} = \frac{3R_H}{4}$$

$$\therefore \left[\lambda = \frac{4}{3R_H}\right]$$

Wave no. of last line of Lyman series

$$\bar{\nu} = R_H \times 1^2\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) \Rightarrow \bar{\nu} = R$$

Balmer Series

- It is the second series of H-spectrum.
- It was found out in 1892 in visible region by Balmer.
- It has $n_1 = 2$ and $n_2 = 3,4,5,$..............
- The wavelength of marginal line of Balmer series $= \frac{n_1^2}{R_H}$ $= \frac{2^2}{R_H} = \frac{4}{R_H}$
- $\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$ where $n_2 > 2$ always.

1^{st} line of balmer series = 3 → 2

last line of balmer series = ∞ → 2

$$(\bar{\nu})\ 1^{st}\ \text{line} = R \times 1\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$$

$$(\bar{\nu})\ \text{last line} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R}{4}$$

Paschen Series

(a) It is the third series of H-spectrum.

(b) It was found out in infrared region by Paschen.

(c) It has $n_1 = 3$ and $n_2 = 4,5,6$ ......

(d) The wavelength of marginal line of Paschen series

$$\frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}.$$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 3$ always.

Brackett Series

(a) It is fourth series of H - spectrum.

(b) It was found out in infrared region by Brackett.

(c) It has $n_1 = 4$ and $n_2 = 5,6,7$ ....

(d) The wavelength of marginal line of brackett series

$$= \frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 4$ always.

Pfund Series

(a) It is fifth series of H-spectrum.

(b) It was found out in infrared region by Pfund.

(c) It has $n_1 = 5$ and $n_2 = 6,7,8$ .... where n_1 is ground state and n_2 is excited state.

(d) The wavelength of marginal line of Pfund series

$$= \frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 5$ always.

Humphrey Series

(a) It is the sixth series of H - spectrum.

(b) It was found out in infrared region by Humphrey.

(c) It has $n_1 = 6$ and $n_2 = 7, 8, 9$ ....

(d) The wavelength of marginal line of Humphrey series

$$= \frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{6^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 6$.

Train Your Brain

Example 18: Calculate wavelength for 2nd line of Balmer series of He^+ ion.

Sol. $\frac{1}{\lambda} = R(2)^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$n_1 = 2 ; n_2 = 4$

$$\frac{1}{\lambda} = R(2^2)\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$\frac{1}{\lambda} = \frac{3R}{4} \quad ; \quad \lambda = \frac{4}{3R}$$

Example 19: The ratio of $(E_2 - E_1)$ to $(E_4 - E_3)$ for He^+ ion is approximately equal to (where E_n is the energy of nth orbit).

(*a*) 10 (*b*) 15

(*c*) 17 (*d*) 12

Sol. $$\frac{\Delta E_{2\to1}}{\Delta E_{4\to3}} = \frac{13.6(2)^2\left[\frac{1}{(1)^2} - \frac{1}{(2)^2}\right]}{13.6(2)^2\left[\frac{1}{(3)^2} - \frac{1}{(4)^2}\right]} \approx 15$$

Example 20: If the binding energy of 2nd excited state of a hydrogen like sample is 24 eV approximately, then the ionisation energy of the sample is approximately.

(*a*) 54.4 eV/atom (*b*) 24 eV/atom

(*c*) 122.4 eV/atom (*d*) 216 eV/atom

Sol. (*d*) $\frac{13.6(Z)^2}{(3)^2} = 24$

I.E. $= 13.6(Z)^2 = (24 \times 9) = 216$ eV/atom

Example 21: If electron make transition from 7th excited state to 2nd orbit in H-atom sample, find the max. number of spectral lines observed.

Sol. $\Delta n = 8 - 2 = 6$

$$\text{spectral lines} = 6\left(\frac{6+1}{2}\right) = 6 \times \frac{7}{2} = 21$$

Example 22: Which transition of the Hydrogen spectrum would have the same length as the Balmer transition, n = 4 to n = 2 of He^+ spectrum?

(*a*) $n_2 = 2$ to $n_1 = 1$ (*b*) $n_2 = 3$ to $n_1 = 1$

(*c*) $n_2 = 4$ to $n_1 = 2$ (*d*) $n_2 = 5$ to $n_1 = 3$

Sol. (*a*) For He^+ ion, we have

$$\frac{1}{\lambda} = R_H Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = [2]^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right] \times R_H$$

$$= \frac{3}{4}R_H \quad \text{...(i)}$$

∴ Now for H atom

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{...(ii)}$$

Equating equs (i) and (ii) we have

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Obviously $n_1 = 1$ and $n_2 = 2$. Hence the transition n = 2 to n = 1 in hydrogen atom will have the same wave length as the transition n = 4 to n = 2 in He^+ species.

Example 23: The shortest wave length in H-spectrum of Lyman series when $R_H = 109678\ cm^{-1}$ is?

(*a*) 1215.67 Å (*b*) 911.7 Å

(*c*) 1002.7 Å (*d*) 1127.30 Å

Sol. (*b*) For Lyman series $n_1 = 1$

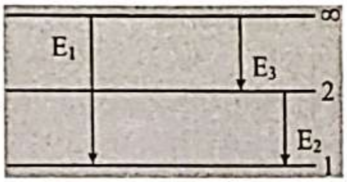
For shortest 'λ' of Lyman series, the energy difference in two levels showing transition should be maximum (i.e. $n_2 = \infty$).

$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = 109678\ cm^{-1}$$

$$\therefore \lambda = 9.117 \times 10^{-8} = 911.7\ Å$$

Example 24: Let ν_1 be the frequency of series limit of lyman series, ν_2 be the frequency of 1st line of lyman series, ν_3 be the frequency of series limit of Balmer series. Then find relation between ν_1, ν_2 and ν_3.

Sol.



$E_1 = E_2 + E_3$

$\Rightarrow h\nu_1 = h\nu_2 + h\nu_3$

$\Rightarrow \nu_1 = \nu_2 + \nu_3$

Concept Application

14. Which electronic transition in the He^+ spectrum would have the same wavelength as the first Lyman transition of hydrogen?

(*a*) (n = 4 to n = 1) (*b*) (n = 4 to n = 2)

(*c*) (n = 3 to n = 2) (*d*) (n = 2 to n = 2)

15. At what atomic number would a transition from n = 2 to n = 1 energy level result in emission of photon of $\lambda = 3 \times 10^{-8}$ m?

(*a*) (Z = 1) (*b*) (Z = 2)

(*c*) (Z = 3) (*d*) (Z = 4)

16. The energy of hydrogen atom in its ground state is -13.6 eV. The energy of the level corresponding to $n = 5$ is:
(*a*) -0.54 eV (*b*) -5.40 eV
(*c*) -0.85 eV (*d*) -2.72 eV

17. The wavelength of a spectral line for an electronic transition is inversely proportional to:
(*a*) Number of electrons undergoing transition.
(*b*) The nuclear charge of the atom.
(*c*) The velocity of an electron undergoing transition.
(*d*) The difference in the energy involved in the transition.

DUAL NATURE OF MATTER (De-Broglie HYPOTHESIS)

(*a*) Einstein had suggested that light can behave as wave as well as like a particle i.e. it has dual character.

(*b*) In 1924, de-Broglie proposed that an electron behaves both as a material particle and as a wave.

(*c*) This proposed a new theory i.e., wave mechanical theory of matter. According to this theory, the electrons, protons and even atoms when in motion possess wave properties.

(*d*) According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation, $\lambda = \frac{h}{mv}$ where h is Planck's constant.

Derivation of de-Broglie Relationship

For a photon,

$$E = \frac{hc}{\lambda} \qquad \text{...(i)}$$

$$E = mc^2 \qquad \text{...(ii)}$$

$$mc^2 = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{h}{mc} = \frac{h}{p}$$

He concluded that as electromagnetic radiation have some associated mass or associated momentum, in the same way every moving particle of mass 'm' and velocity 'v' is associated with waves and these associated waves are known as matter waves or de-Broglie's waves.

$$\lambda = h/mv = h/p$$

Derivation of Bohr's postulate of quantisation of angular momentum from de-Broglie's Equations: According to de-Broglie moving electron is associated with waves which must be completely in phase and therefore only those orbits are possible where circumference of the orbit is integral multiple of λ i.e. $2\pi r = n\lambda$, where n is the no. of waves.

$$2\pi r = \frac{nh}{mv} \Rightarrow mvr = \frac{nh}{2\pi}$$

From the above expression it can be commented that **number of waves in a shell in a complete revolution = shell no.**

❖ **Calculation of de-Broglie wavelength if K.E. of the particle is E:**

$$E = \frac{1}{2}mv^2 \Rightarrow 2E = mv^2$$

$$2mE = m^2v^2 = p^2 \Rightarrow p = \sqrt{2mE}$$

$$\frac{h}{\lambda_{dB}} = \sqrt{2mE} \Rightarrow \lambda_{dB} = \frac{h}{\sqrt{2mE}}$$

If a charged particle at rest (having charge 'q') is accelerated by potential difference 'V' volt then:

$$\lambda_{dB} = \frac{h}{\sqrt{2mqV}},$$

$$\boxed{\lambda_{dB} = \sqrt{\frac{150}{V}}\,\text{Å} \quad \text{(Only for electron)}}$$

Train Your Brain

Example 25: Calculate λ_{dB} of electron have K.E. 3eV.

Sol. $\lambda_{dB} = \sqrt{\frac{150}{K.E.}} = \sqrt{\frac{150}{3}} = \sqrt{50}\,\text{Å} = 7.07\text{Å}$

Example 26: Calculate the wavelength of a moving electron having 4.55×10^{-25} J of kinetic energy.

Sol. Kinetic energy $= \left(\frac{1}{2}mv^2\right) = 4.55 \times 10^{-25}$ J

$$\therefore \quad \lambda = \frac{h}{\sqrt{2 \times m \times K.E.}}$$

$$\text{or } \lambda = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 4.55 \times 10^{-25}}} = 7.28 \times 10^{-7} \text{ meter}$$

Concept Application

18. An α-particle is accelerated through a potential difference of V volts from rest. The de-Broglie's wavelength associated with it is:
(*a*) $\sqrt{\frac{150}{V}}$Å (*b*) $\frac{0.286}{\sqrt{V}}$Å
(*c*) $\frac{0.101}{\sqrt{V}}$Å (*d*) $\frac{0.983}{\sqrt{V}}$Å

19. What possibly can be the ratio of the de-Broglie wavelengths for two electrons each having zero initial energy and accelerated through 50 volts and 200 volts?
(*a*) 3 : 10 (*b*) 10 : 3 (*c*) 1 : 2 (*d*) 2 : 1

HEISENBERG'S UNCERTAINTY PRINCIPLE

The exact position and momentum of a fast moving microscopic particle cannot be calculated precisely at the same moment of time. If Δx is the error in the measurement of position of the particle and if Δp is the error in the measurement of momentum of the particle, then:

$$\boxed{\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot (m\Delta v) \geq \frac{h}{4\pi}}$$

where, Δx = uncertainty in position
Δp = uncertainty in momentum
h = Planck's constant
m = mass of the particle
Δv = uncertainty in velocity

If the position of a particle is measured precisely, i.e. $\Delta x \to 0$ then $\Delta p \to \infty$.

If the momentum of the particle is measured precisely. i.e. $\Delta p \to 0$ then $\Delta x \to \infty$.

This is because of a principle of optics that if a light of wavelength 'λ' is used to locate the position of a particle then minimum error in the position measurement will be ± λ amount.

i.e. $\Delta x = \pm \lambda$

If $\Delta x \to 0$; $\lambda \to 0$

But, $p = \frac{h}{\lambda} \Rightarrow p \to \infty$

To make $\Delta x \to 0$, $\lambda \to 0$ a photon of very small wavelength i.e., high energy is required to locate it.

∴ When this photon will collide with the electron then momentum of electron will get changed by a large amount.

$\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$ (Multiplied & divided by Δt)

$$\frac{\Delta p}{\Delta t}\Delta t \cdot \Delta x \geq \frac{h}{4\pi}$$

($\frac{\Delta p}{\Delta t}$ = rate of change in momentum = F)

$$F \cdot \Delta x \cdot \Delta t \geq \frac{h}{4\pi}$$

$$\boxed{\Delta E \cdot \Delta t \geq \frac{h}{4\pi}}$$

ΔE ⟶ uncertainty in energy

Δt ⟶ uncertainty in time

- In terms of uncertainty in energy ΔE, and uncertainty in time Δt, this principle is written as,

  $$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

- Heisenberg replaced the concept of definite orbits by the concept of probability.

Train Your Brain

Example 27: A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Sol. The uncertainty in the speed is 2%,

i.e., $45 \times \frac{2}{100} = 0.9\ \text{m s}^{-1}$. Using the equation

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 40 \times 10^{-3}\,(0.9\ \text{m s}^{-1})}$$

$= 1.46 \times 10^{-33}$ m

This is nearly ~10^{18} times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Example 28: The uncertainty in measuring speed of a particle is zero. Uncertainty in measuring its position will be

(*a*) Zero
(*b*) $\frac{h}{4\pi}$
(*c*) $\frac{h}{4\pi m}$
(*d*) Infinite

Sol. (*d*) $\Delta x = \frac{h}{4\pi \times m \times \Delta v}$

or $\Delta x = \infty$ as $\Delta v = 0$

Example 29: The mass of a particle is 10^{-10} g and its diameter is 10^{-4} cm. If its speed is 10^{-6} cm/s with 0.0001% uncertainty in measurement, the minimum uncertainty in its position is

(*a*) 5.28×10^{-8} m
(*b*) 5.28×10^{-7}
(*c*) 5.28×10^{-6} m
(*d*) 5.28×10^{-9} m

Sol. (*a*) $m = 10^{-10}$ g or $m = 10^{-13}$ kg

$\Delta v = 10^{-6} \times 10^{-2} \times 0.0001 \times 10^{-2}\ \text{m/s} = 10^{-14}\ \text{m/s}$

According to Heisenberg's Uncertainty Principle

$$\Delta x \times m\Delta v = \frac{h}{4\pi} \text{ or}$$

$$\Delta x = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-13} \times 10^{-14}}\,m \text{ or } \Delta x = 5.28 \times 10^{-8}\,m$$

Concept Application

20. The uncertainty in the momentum of an electron is $1.0 \times 10^{-5}\ \text{kg m s}^{-1}$. The uncertainty in its position will be: ($h = 6.626 \times 10^{-34}$ Js)

(*a*) 1.05×10^{-28} m
(*b*) 1.05×10^{-26} m
(*c*) 5.27×10^{-30} m
(*d*) 5.25×10^{-28} m

21. If uncertainty in position and momentum of a particle is numerically equal, then the minimum uncertainty in speed of the particle is

(*a*) $\sqrt{\frac{h}{2\pi}}$
(*b*) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$
(*c*) $\sqrt{\frac{h}{\pi}}$
(*d*) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$

22. Uncertainty in the position of an electron (mass $= 9.1 \times 10^{-31}$ kg) moving with a velocity 300 m/s, accurate up to 0.001 %, will be ($h = 6.3 \times 10^{-34}$ Js)

(*a*) 5.76×10^{-2} m (*b*) 1.92×10^{-2} m

(*c*) 3.84×10^{-2} m (*d*) 19.2×10^{-2} m

THE QUANTUM/WAVE MECHANICAL MODEL

- Quantum mechanics is a theoretical science that deals with the study of motions of the microscopic objects that have both observable wave-like and particle-like properties.
- It specifies the laws of motion that these objects obey.
- When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.
- Quantum mechanical model of atom is the picture of structure of the atom, which emerges from the application of the Schrödinger equation to atoms.
- For a particle whose energy does not vary with time, the Schrodinger equation may be written as

$$\hat{H}\Psi = E\Psi$$

- where $\hat{H}$ = Hamiltonian or Total energy operator, ψ = wave function

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m(E-V)}{h^2}\psi = 0$$

where x, y and z are Cartesian Co-ordinates, m = mass of the electron,

E = Total energy of the electron, V = P.E. of the electron,

ψ = Wave function of the electron

- For a given system for which V and m are known, we can use the Schrödinger equation to obtain value of E (the allowed energies of the particle) & ψ (the wave function).
- For H-atom, P.E. $(V) = -\frac{Ke^2}{r}$
- Schrodinger's wave equation becomes

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m\left(E+\frac{Ke^2}{r}\right)}{h^2}\psi = 0$$

- The wave function itself has no physical meaning, but ψ^2 is a probability density and for this to be the case, ψ must have certain properties:
  - It must be finite for all values of x;
  - It can only have one value for any value of x;
  - And $\frac{d\psi}{dx}$ must vary continuously as x varies.
- ψ must be continuous, have a continuous slope, be single-valued, & be square integrable.
- The results (solutions) of wave equation are
  - The wave function is a solution of the Schrodinger equation and describes the behavior of an electron in region of space called the atomic orbital.
  - We can find energy values that are associated with particular wave functions.
  - The quantization of energy levels arises naturally from the Schrodinger equation.
  - A wave function ψ is a mathematical function that contains detailed information about the behavior of an electron.
  - An atomic wave function consists of a radial component, R (r), and an angular component, A (β, ϕ).
  - The region of space defined by a wave function is called an atomic orbital.

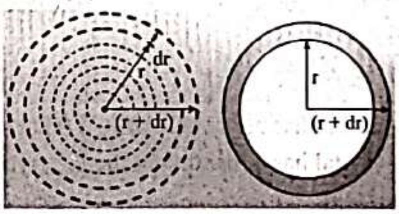
Born Interpretation of Wave Equation

- A principal tenet of quantum mechanics is that the wave function contains all the dynamic information about the system it describes.
- **In the words of Born:** If the wave function of a particle has the value ψ at some point x, then probability of finding the particle between x and (x + dx) is proportional to $|\psi|^2$ dx.
- "For a three dimensional wave function of a particle, if the wave function of a particle has the value ψ at some point, then probability of finding a particle in a small volume (dV) around that point is $|\psi|^2$ dV".
- **The wave function ψ is a probability amplitude that means its square modulus ($|\psi|^2$) is a probability density.**
- The physical significance of ψ is difficult to understand, but $|\psi|^2$ has a clear physical significance of being the probability density (probability per unit volume) of the location of particle.

Radial Probability Function

- Radial probability distribution function = R^2dV.

  (where R = radial wave function)
- In order to find the value of dV, the entire space of the electron orbital around the nucleus is supposed to be divided into small imaginary concentric shells of very small thickness dr, each.



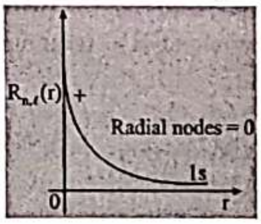
RADIAL WAVE FUNCTION FOR H-LIKE ATOMS

- $R_{n,\ell}$ = Constant × polynomial × Exponential.

(1) $\boxed{R_{n,\ell}\text{ (r) v/s r plots:}}$

(*i*) 1s-orbital:

$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} \times 1 \times e^{-Zr/a_0}$$



- 1s - orbital has a finite value of $R_{n,\ell}$ (r) at nucleus.

(*ii*) 2s-orbital:

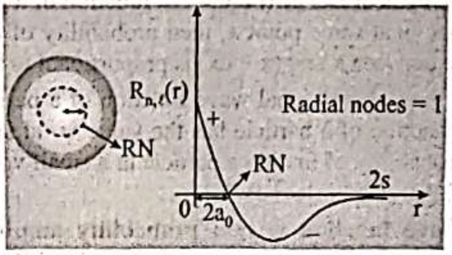
$$R_{2,0}=\left(\frac{Z}{a_0}\right)^{3/2}\frac{1}{2\sqrt{2}}\times\left(2-\frac{Zr}{a_0}\right)\times e^{-Zr/2a_0}$$

(*a*) If $2>\frac{Zr}{a_0}$, then $R_{2,0}$ is + ve.

(*b*) If $\frac{Zr}{a_0}>2$, then $R_{2,0}$ is – ve.

(*c*) If $\frac{Zr}{a_0}=2$, then $R_{2,0}$ is 0.

At Radial node, $r=\frac{2a_0}{Z}$

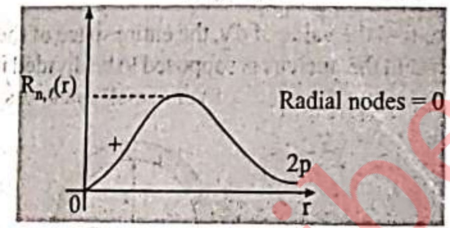


2s-orbital has a finite value of $R_{n,\ell}$ (r) at nucleus.

2s-orbital wave function also decays exponentially but its decay is slower than 1s-orbital.

(*iii*) 2p-subshell:

$$R_{2,1}=\left(\frac{Z}{a_o}\right)^{3/2}\frac{1}{2\sqrt{6}}\times\left(\frac{Zr}{a_o}\right)\times e^{-Zr/2a_0}$$

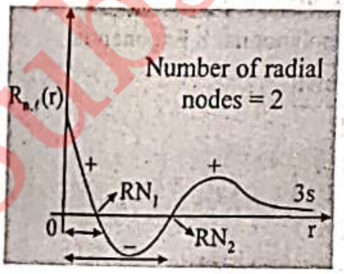


2p - orbital has zero value of $R_{n,\ell}$ (r) at nucleus.

2p - orbital has a maxima in the $R_{n,\ell}$(r) v/s r plot.

(*iv*) 3s-orbital:

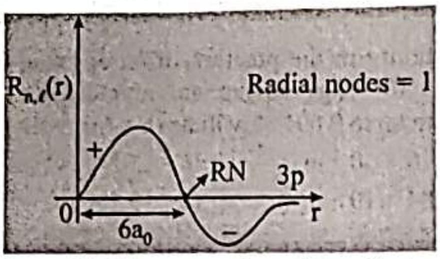
$$R_{3,0}=\left(\frac{Z}{a_0}\right)^{3/2}\frac{2}{81\sqrt{3}}\times\left(27-18\frac{Zr}{a_0}+\frac{2Z^2r^2}{a_0^2}\right)\times e^{-Zr/3a_0}$$



3s - orbital has a finite value of $R_{n,\ell}$ (r) at nucleus.

(*v*) 3p-subshell:

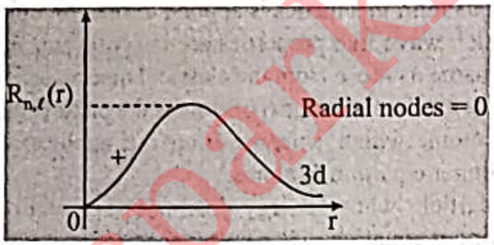
$$R_{3,1}=\left(\frac{Z}{a_0}\right)^{3/2}\frac{4}{81\sqrt{6}}\times\left(6\frac{Zr}{a_0}-\frac{Z^2r^2}{a_0^2}\right)\times e^{-Zr/3a_0}$$



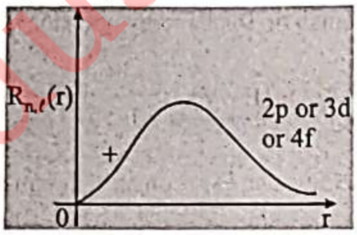
3p - orbital has zero value of $R_{n,\ell}$ (r) at nucleus.

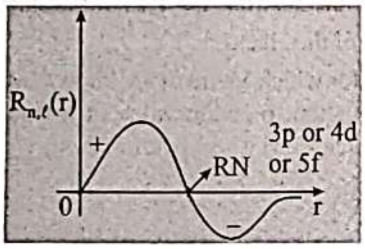
(*vi*) 3d-subshell:

$$R_{3,2}=\left(\frac{Z}{a_0}\right)^{3/2}\frac{4}{81\sqrt{30}}\times\frac{Z^2r^2}{a_0^2}\times e^{-Zr/3a_0}$$



3d - orbital has zero value of $R_{n,\ell}$ (r) at the nucleus.



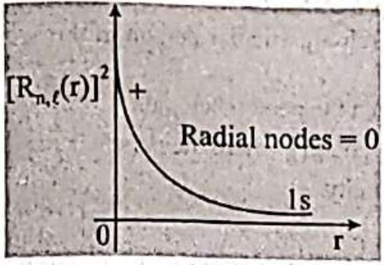


- For all orbitals other than s-orbital, $R_{n,\ell}$ (r) = 0 at the nucleus.
- For all 1s - orbitals, $R_{n,\ell}$ (r) is always positive.
- For the first orbital of other types (i.e. 2p, 3d, 4f etc), $R_{n,\ell}$ (r) is +ve everywhere except at the origin.
- For the second orbital of a given type (i.e. 2s, 3p, 4d, 5f etc.), $R_{n,\ell}$ (r) may be + ve or – ve but the radial wave function has only 1 sign change, i.e. they have 1 radial node.
- For the third orbital of a given type (i.e. 3s, 4p, 5d, 6f etc.), $R_{n,\ell}$ (r) may have 2 sign changes i.e. they have 2 radial nodes.

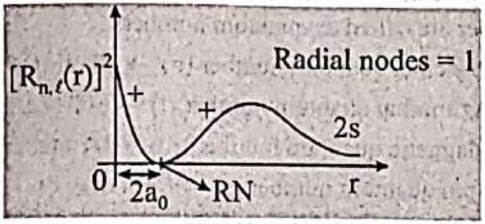
(2) $\boxed{[R_{n,\ell}(r)]^2 \text{ v/s r plots:}}$

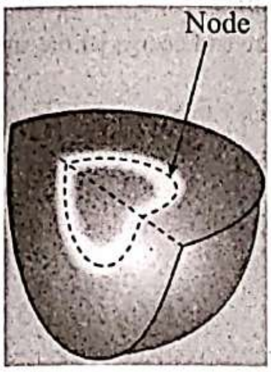
$[R_{n,\ell}(r)]^2$ would always be +ve, irrespective of the sign of $R_{n,\ell}$ (r) for a given value of r. R^2 represents the probability density of finding electron at a particular point in space.

(i) 1s – orbital:

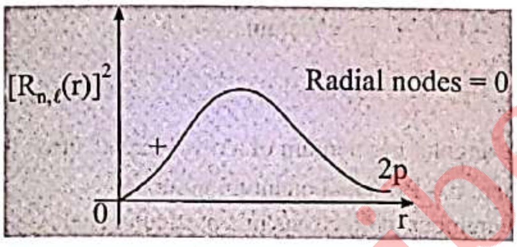


(ii) 2s – orbital:

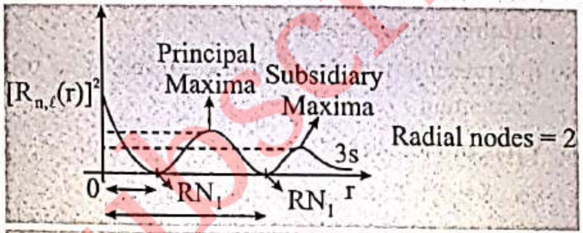


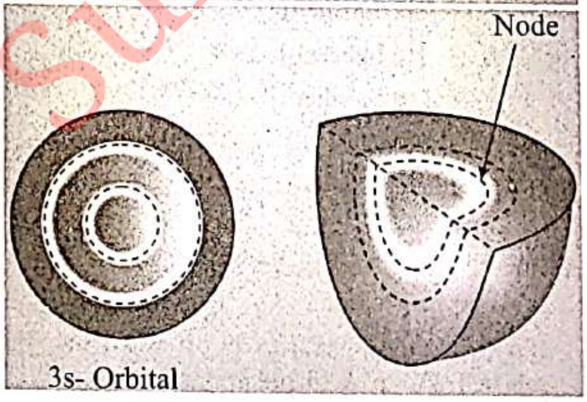


(iii) 2p – subshell:

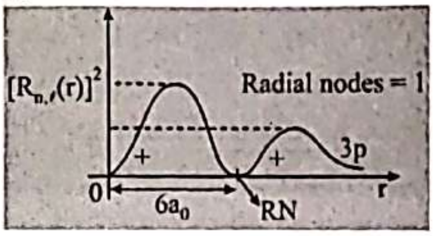


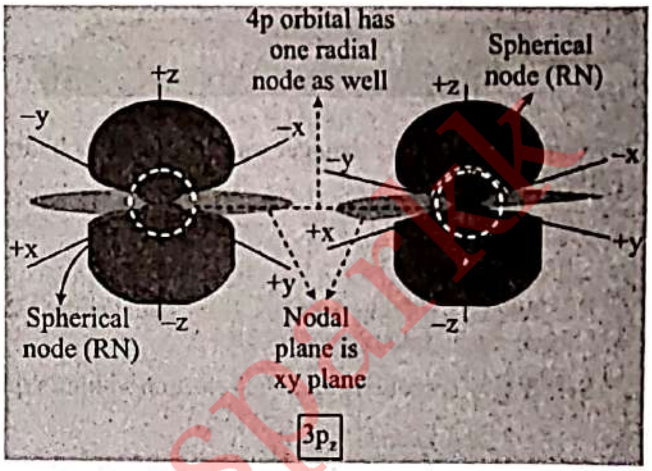
(iv) 3s -orbital:



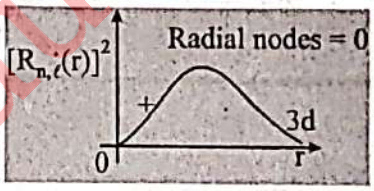

Node
3s- Orbital

(v) 3p-subshell:




4p orbital has one radial node as well
Spherical node (RN)
+z
–y
–x
–y
+x
+x
+y
–z
Spherical node (RN)
Nodal plane is xy plane
+z
–x
+y
–z
$3p_z$

(vi) 3d-subshell:



Key Note

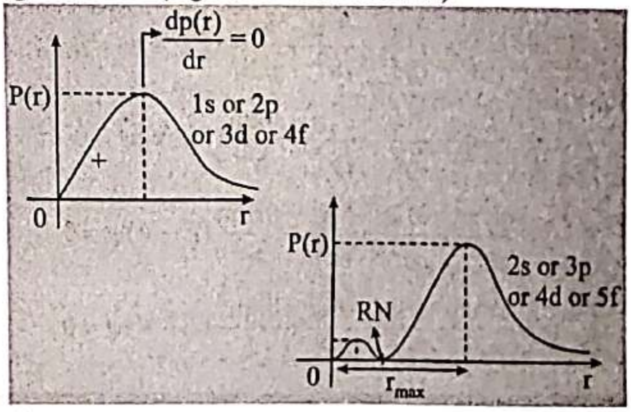
- First maxima is higher than second and second is higher than third.
- **$R_{n,1}$ (r) v/s r plot, R^2 v/s r plot & $4\pi r^2 R^2$ v/s r plot are all same for '2p' orbital, '3d' orbital, '4f' orbital etc.**

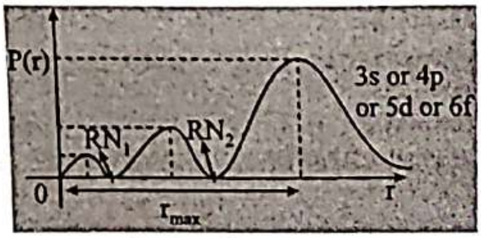
(3) $4\pi r^2 [R_{n,1}(r)]^2$ v/s r plots:

- Radial distribution function or radial probability distribution function (RPDF)

  $= p(r)\,dr = 4\pi r^2 [R_{n,1}(r)]^2\,dr$

  The radial distribution is the probability function of choice to determine the most likely radius to find the electron for a given orbital (regardless of its direction).





Train Your Brain

Example 30: The Schrodinger wave equation for hydrogen atom is

$$\Psi_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

Where a_0 is Bohr's radius. If the radial node in 2s be at r, then find r in terms of a_0.

Sol. Ψ_{2s}^2 = Probability of finding electron within 2s sphere

$\Psi_{2s}^2 = 0$ at node

$$\therefore \left(2-\frac{r}{a_0}\right)^2 = 0 \Rightarrow \left(2-\frac{r}{a_0}\right) = 0 \Rightarrow 2 = \frac{r}{a_0} \Rightarrow r = 2a_0$$

Concept Application

23. For an orbital in B^{+4} radial function is:

$$R(r) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{4}}(4-\sigma)\sigma\ e^{-\sigma/2}$$

where $\sigma = \frac{Zr}{a_0}$ and $a_0 = 0.529$ Å ; Z = atomic number,
r = radial distance from nucleus.
Find the distance (in Å) of radial node of orbital from the nucleus.

24. The correct time independent Schrödinger's wave equation for an electron with E as total energy and V as potential energy is :

(a) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2}{mh^2}(E-V)\psi = 0$

(b) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi m}{h^2}(E-V)\psi = 0$

(c) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0$

(d) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi m^2}{h}(E-V)\psi = 0$

QUANTUM NUMBER

As we know to search a particular person in this world 4 things are needed:

1. Country to which the person belongs.
2. The city in that country where the person is residing.
3. The area in that city.
4. House number.

Similarly to locate the position of an electron in the atom 4 identification number are required and these identification number are called as quantum numbers.

1. Principal quantum number (n) → Shell (Orbit)
2. Azimuthal quantum number (l) → Sub shell
3. Magnetic quantum number (m) → Orbital
4. Spin quantum number (s) → Spin of e$^-$

1. Principal quantum number:

It represents the name, size and energy of the shell to which e$^-$ belongs.

- The value of n lies between 1 to ∞.
  i.e n = 1,2,3,4.............. ∞ corresponding name of shells are K, L, M, N, O, ...
- Greater the value of n, greater is the distance from the nucleus.
  $r = 0.529 \times \frac{n^2}{z}$ Å
  $r_1 < r_2 < r_3 < r_4 < r_5$ ....
- Greater the value of n, greater is the energy of shell.
  $E = -13.6 \times \frac{z^2}{n^2}$ eV/atom
  $E_1 < E_2 < E_3 < E_4$ ....
- The angular momentum of a revolving electron is $mvr = \frac{nh}{2\pi}$.
  Where n = Principal quantum number.
- The number of electrons in a particular shell is equal to $2n^2$.

2. Azimuthal quantum number / Angular quantum number/ Secondary quantum number /Subsidiary quantum number: Represented by 'l'

- It represents the shape of the subshell and orbital angular momentum.
- Value of ℓ between 0 to (n – 1).
  i.e. ℓ = 0,1,2 .... (n – 1).
  ℓ = 0(s Subshell)
  ℓ = 1(p Subshell)
  ℓ = 2(d Subshell)
  ℓ = 3(f Subshell)
- If n = 1 then ℓ = 0 ⇒ 1s i.e. in n = 1 shell, only one subshell 's' is present.

  If n = 2 then ℓ = 0,1 ⇒ 2s, 2p i.e. in n = 2 shell, two subshell 's' & 'p' are present.

  If n = 3 then ℓ = 0,1,2 ⇒ 3s, 3p, 3d i.e. in n = 3 shell, three subshell 's', 'p' & 'd' are present.

If $n = 4$ then $\ell = 0,1,2,3 \Rightarrow$ 4s, 4p, 4d, 4f i.e. in $n = 4$ shell; four subshell 's', 'p', 'd' & 'f' are present.

- If the value of n is same then the order of energy of the various subshell will be:

  $s < p < d < f$

  $4s < 4p < 4d < 4f$, $3s < 3p < 3d$, $2s < 2p$

- If value of ℓ is same but value of n is different then the order of energy will be:

  $1s < 2s < 3s < 4s < 5s < 6s$

  $3d < 4d < 5d < 6d$

  $4p < 5p < 6p$

- The orbital angular momentum $= \sqrt{\ell(\ell+1)}\ \dfrac{h}{2\pi}$ or $\sqrt{\ell(\ell+1)}\hbar\ \left\{\because \hbar = \dfrac{h}{2\pi}\right\}$

  Orbital angular momentum : For s subshell = 0

  For p Subshell $= \sqrt{2}\dfrac{h}{2\pi}$ or $\sqrt{2}\hbar$.

- The number of electron in a particular subshell is equal to $2(2\ell + 1)$.

  for s subshell number of electrons = 2 e^-

  for p subshell number of electrons = 6 e^-

  for d subshell number of electrons = 10 e^-

  for f subshell number of electrons = 14 e^-

- Shape of the subshell:

  s → spherical
  p → dumb bell shape
  d → double dumb bell shape
  f → complex shape

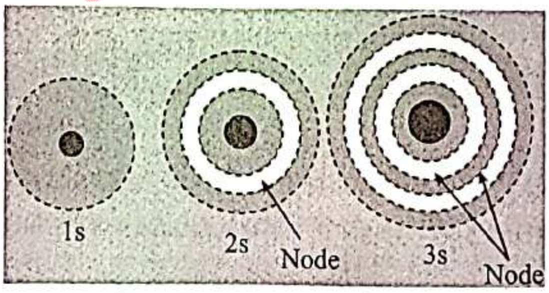
3. **Magnetic quantum number /Orientation quantum number (m):** It represents the shape of different orbitals and the orientation of electron cloud (orbital).

Under the influence of magnetic field each subshell is further subdivided into orbitals (The electron cloud is known as orbital). Magnetic quantum number describe these different distribution of electron clouds.

Value of m = all integral value from $-\ell$ to $+\ell$ including zero.
i.e. Value of $m = -\ell$ .... 0 .... $+\ell$

Case-I: If $\ell = 0$ then $m = 0$ it implies that s subshell has only one orbital called as "s orbital".

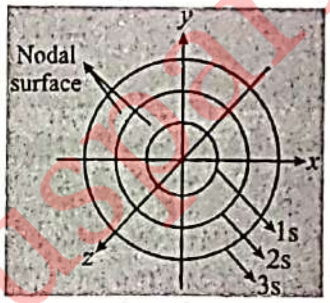
Shapes of s-orbitals: The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding ns electron is same in all directions from the nucleus. The size of the orbital depends on the value of principal quantum number, there is one spherically symmetrical orbital. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 3s, but all are spherical in shape as shown in figure.



Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below:

(*i*) The probability of 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero and increases again and then decreases as the distance from the nucleus increases. The intermediate region (a spherical shell), where the probability is zero is called a nodal surface or simply node. Thus, 2s-orbital differs from 1s-orbital in having one node within it. Similarly, 3s orbital has two nodes. In general, any ns orbital has (n -1) nodes.

(*ii*) The size and energy of the s-orbital increases as the principal quantum number increases, i.e., the size and energy of s-orbital increases in the order $1s < 2s < 3s$ ....



- The s orbital of higher energy levels are also symmetrically spherical and can be represented as follows:

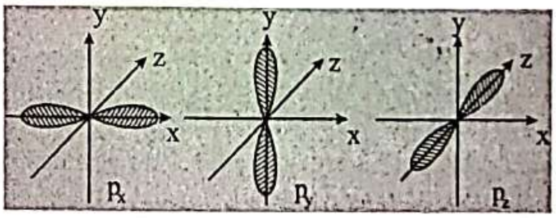
Case-II: If $\ell = 1$ (p - subshell) then $m = -1, 0, 1$

It implies that, p subshell have three orbitals called as p_x, p_y and p_z.

Shape of p-orbitals: There are three p-orbitals, commonly referred to as p_x, p_y and p_z. These three p-orbitals, possess equivalent energy. They, however, differ in their direction & distribution of the charge.

These three p-orbitals are situated at right angle to one another and are directed along x, y and z axis (figure).

Each p orbital has dumb bell shape (2 lobes which are separated from each other by a point of zero probability called nodal point or node or nucleus).



The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.

Each p orbital of higher energy level are also dumb bell shape but they have spherical nodal surface.

Nodal surface:

Orbital	No. of spherical nodes
2 p_x	0
3 p_x	1
4 p_x	2
np_x	$(n-2)$

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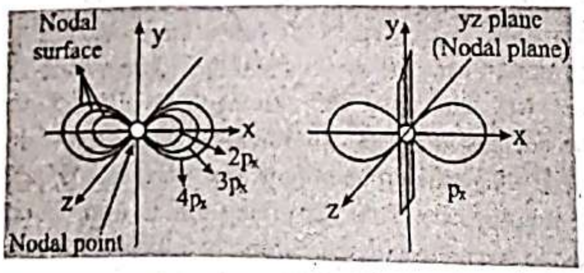
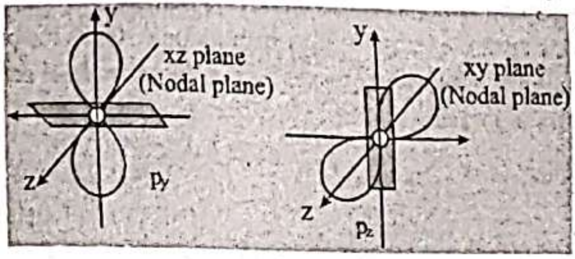
Nodal Plane:

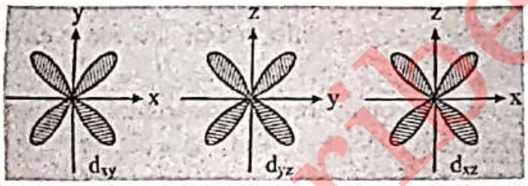
Orbital	Nodal plane
p_x	yz plane
p_y	xz plane
p_z	xy plane

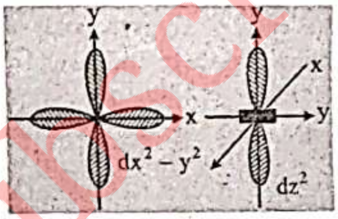




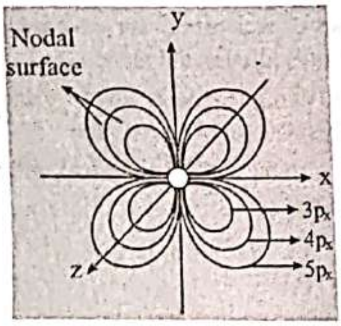
Case-III: When $\ell = 2$, 'm' has five values $-2, -1, 0, +1, +2$. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ contain four lobes while fifth orbital d_{z^2} consists of only two lobes. The lobes d_{xy} orbital lie between x and y axis. Similar is the case for d_{yz} and d_{xz}. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axis while the two lobes of d_{z^2} orbital are lying along z axis and contain a ring of negative charge surrounding the nucleus in xy plane. Geometry of d orbital is Double Dumb bell.

Shape of d–orbitals: It implies that d subshell has 5 orbitals i.e. five electron cloud and can be represented as follows.





Each d-orbital of higher energy level are also double dumb bell shaped but they have spherical nodal surface.



(i) Nodal Point → 1

(ii) Nodal Surface → $3d_{xy}$ → 0; Nodal surface
$4d_{xy}$ → 1; Nodal surface
$5d_{xy}$ → 2; Nodal surface
nd_{xy} → $(n-3)$; Nodal surface

Number of nodal surface $= n - \ell - 1$

(iii) Nodal plane : d_{xy} → xz & yz nodal plane.
d_{xz} → xy & zy nodal plane.
d_{zy} → zx & yx nodal plane.
$d_{x^2-y^2}$ → two, nodal planes at angles 45° to x and y axes
d_{z^2} → two angular nodes (nodal cones)

Note: Orbitals of d subshell are Equivalent in energy.

Case-IV:

f subshell : When $\ell = 3$ (f subshell)

The structure of f-orbital is very complex.

The number of seven values of $m = -3, -2, -1, 0, 1, 2, 3$ for f-orbitals in f subshell show that f subshell has 7 orbitals which are equivalent in energy.

Representation of the orbitals :

$$\text{s subshell} \rightarrow \overset{s}{\boxed{s}}$$

$$\text{p subshell} \rightarrow \overset{p}{\boxed{p_x \mid p_y \mid p_z}}$$

$$\text{d subshell} \rightarrow \overset{d}{\boxed{d_{xy} \mid d_{yz} \mid d_{z^2} \mid d_{xz} \mid d_{x^2y^2}}}$$

$$\text{f subshell} \rightarrow \overset{f}{\boxed{f_{x^3} \mid f_{y^3} \mid f_{z^3} \mid f_{xyz} \mid f_{x(y^2-z^2)} \mid f_{y(z^2-x^2)} \mid f_{z(x^2-y^2)}}}$$

4. Spin Quantum number (s):

It represents the direction of electron spin around its own axis.

- For clock wise spin/spin up (↑) electron → ±½.
  For anti-clock wise spin/spin down (↓) electron → ∓½.
- Spin angular momentum of an $e^- = \sqrt{s(s+1)}.\dfrac{h}{2\pi}$.
  or $\sqrt{s(s+1)}\,\hbar$
- Each orbital can accommodate 2 electrons with opposite spin or spin paired.
  Correct $\boxed{\uparrow\downarrow}$ spin paired
  Wrong $\boxed{\uparrow\uparrow}$ spin paired

Train Your Brain

Example 31: For 5 d_{z^2}, calculate the value of n, l, m and s.

Sol. $n = 5$, $\ell = 2$, $m = 0$, $s = +\dfrac{1}{2}$ or $-\dfrac{1}{2}$

D.P.P = 7 → 1|2|4|5|6|9|10

H.W **Example 32:** Which of the following set of Quantum number is not possible?

(a) $n = 3, \ell = +2, m = 0, s = +\frac{1}{2}$

(b) $n = 3, \ell = 0, m = 0, s = -\frac{1}{2}$

[✓ (c)] $n = 3, \ell = 0, m = 1, s = +\frac{1}{2}$

(d) $n = 3, \ell = 1, m = 0, s = -\frac{1}{2}$

Sol. (c) For s-subshell, $l = 0$ then m should be 0

H.W **Example 33:** The number of orbitals of g-type is

(a) 5 (b) 7 [✓ (c)] 9 (d) 11

Sol. (c) For g - subshell, $l = 4$.
Therefor no. of orbital $= -l$ to $+l$.
i.e. –4 to +4 (including zero).
Hence in g-subshell, 9 orbitals are present.

H.W

Concept Application

25. Number of orbitals represented by $n = 3$, $l = 2$ and $m = +2$ is

[✓ (a)] 1 (b) 2 (c) 3 (d) 4

26. An electron that has the quantum numbers $n = 3$ and $m = 2$

(a) Must have spin quantum number value, + 1/2.

[✓ (b)] Must have $l = 2$, 3 or 4

(c) Must have $l = 0$, 1 or 2

[✓ (d)] Must have $l = 2$

27. If an electron has spin quantum number of + ½ and magnetic quantum number of –1, it cannot be present in

[✓ (a)] s-orbital (b) p-orbital

(c) d-orbital (d) f-orbital

28. In which of the following orbital, electron will be closest to the nucleus?

[✓ (a)] 6s P [✓ (b)] 4f N (c) 5d O (d) 6p P

29. Possible set of electrons for which: $n = 4$, $l = 3$ and $\boxed{s = +\frac{1}{2}}$ is

[✓ (a)] 14 [✓ (b)] 7 (c) 5 (d) 10

Rules for Filling Subshell

1. Aufbau Principle.

2. (n + l) rule.

3. Hund's maximum spin multiplicity principle.

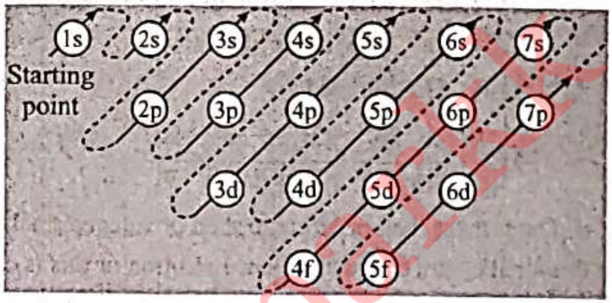
4. Pauli's exclusion principle.

1. **Aufbau Principle:** Aufbau is a German word and its meaning is 'Building up'.

Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the energies of various subshell.

Principle: The subshell with minimum energy is filled up first when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.

The sequence in which various subshell are filled are as follows.



Electronic configuration of Atoms

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$, ...

For Ex.

${}_1H \rightarrow 1s^1$
${}_2He \rightarrow 1s^2$
${}_3Li \rightarrow 1s^2, 2s^1$
${}_4Be \rightarrow 1s^2, 2s^2$
${}_5B \rightarrow 1s^2, 2s^2, 2p^1$
${}_6C \rightarrow 1s^2, 2s^2, 2p^2$
${}_7N \rightarrow 1s^2, 2s^2, 2p^3$
${}_8O \rightarrow 1s^2, 2s^2, 2p^4$
${}_9F \rightarrow 1s^2, 2s^2, 2p^5$
${}_{10}Ne \rightarrow 1s^2, 2s^2, 2p^6$
${}_{11}Na \rightarrow 1s^2, 2s^2, 2p^6, 3s^1$
${}_{12}Mg \rightarrow 1s^2, 2s^2, 2p^6, 3s^2$
${}_{13}A\ell \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
${}_{14}Si \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
${}_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
${}_{16}S \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
${}_{17}Cl \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
${}_{18}Ar \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
${}_{19}K \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}_{20}Ca \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
${}_{21}Sc \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
${}_{22}Ti \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
${}_{23}V \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
${}_{24}Cr \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \underline{4s^1}, 3d^5$
[Exception]
${}_{25}Mn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
${}_{26}Fe \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

$_{27}Co \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$

$_{28}Ni \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

$_{29}Cu \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$
[Exception]

$_{30}Zn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Electronic configuration can be written by following different methods:

$_{26}Fe \rightarrow$ (1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
(2) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$
(3) $1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$
(4) $[Ar]\ 4s^2\ 3d^6$

$$_{26}Fe \rightarrow 1s^2\ \underbrace{2s^2 2p^6}_{(n-2)}\ \underbrace{3s^2 3p^6 3d^6}_{(n-1)}\ \underbrace{4s^2}_{n}$$

n → Outer most shell or ultimate shell or valence shell. In this shell e^- are called as valence electron or this is called core charge.

(n – 1) → Penultimate shell or core or pre valence Shell.

(n – 2) → Pre penultimate shell.

If we remove the last n shell (ultimate shell) then the remaining shell collectively be called as Kernel.

Ex. $_{26}Fe \rightarrow \underbrace{1s^2 2s^2 2p^6 3s^2 3d^6 3p^6}_{\text{Kernel}}\ 4s^2$

2. (*n* + *l*) rule: According to it the sequence in which various subshell are filled up can also be determined with the help of (n + *l*) value for a given subshell.

Principle of (n + *l*) rule: The subshell with lowest (n + ℓ) value is filled up first, When two or more subshell have same (n + ℓ) value then the subshell with lowest value of n is filled up first.

Sub shell	n	ℓ	n+ℓ	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)
4d	4	2	6	(1)
5p	5	1	6	(2)
6s	6	0	6	(3)

Order of energy : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$, ...

3. Hund's Maximum Spin Multiplicity Rule: (Multiplicity: Many of the same kind).

According to Hund's rule "electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electron with parallel spin".

Thus the orbital available in the subshell are first filled singly with parallel spin electron before they begin to pair this means that pairing of electrons occurs with the introduction of second electron in 's' subshell, fourth electron in 'p' subshell, 6th electron in 'd' Subshell & 8th e^- in 'f' subshell.

Ex.

	$1s^2$	$2s^2$	$2p$
$_5B \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^1$ $\boxed{\uparrow}\boxed{\ }\boxed{\ }$
$_6C \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^2$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }$
$_7N \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^3$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$
$_8O \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^4$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$
$_9F \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^5$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$
$_{10}Ne \rightarrow$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$2p^6$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

4. Pauli's Exclusion principle: In 1925 Pauli stated that "no two electron in an atom can have same values of all four quantum numbers. i.e. An orbital can accommodates maximum 2 electrons with opposite spin".

Ex.1. $_6C^{12} \rightarrow 1s^2\ 2s^2\ 2p^2$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }$

			$p_x\ p_z\ p_y$
n	1	2	2
ℓ	0	0	1
m	0	0	– 1, 0, +1
s	+½, –½	+½, –½	+½, +½,

Exception of Aufbau principle: In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple region behind this is that half filled & fully filled subshell have got extra stability.

Ex.1 $_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$
(wrong configuration)

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }$

$_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
(right configuration)

$\boxed{\uparrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Ex.2 $_{29}Cu \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$
(wrong configuration)

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

$_{29}Cu \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$ (right configuration)

$\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

EXTRA STABILITY OF HALF-FILLED & FULLY FILLED SUBSHELLS

Symmetrical Distribution of Electrons

- It is well known that symmetry leads to stability.
- The completely filled or half-filled sub-shells have symmetrical distribution of electrons in them and are therefore more stable.

Exchange Energy

- The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a sub-shell.
- These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy.
- The number of exchanges that can take place is maximum when the sub-shell is either half-filled or completely filled.
- As a result the exchange energy is maximum and so is the stability.
- You may notice that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible.
- **In other words, the extra stability of half-filled and completely filled sub-shell is due to:**
- **Relatively small shielding**
- **Smaller coulombic repulsion energy**
- **Larger exchange energy**
- **Symmetrical distribution of electrons**

Train Your Brain

Example 34: Calculate the number of unpaired e^- in Cr.

Sol. $_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

In $_{24}Cr$, $6e^-$ are unpaired.

Example 35: The number of unpaired e^- in Cr^{+3} is:

Sol. $Cr^{+3} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^3$

In Cr^{+3}, $3e^-$ are unpaired.

Example 36: The number of unpaired e^- in 3d subshell of Cr^{+3} is:

Sol. $Cr^{+3} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^3$

Therefore number of unpaired electron in 3d subshell is 3.

Example 37: The number of unpaired e^- in Fe^{+2} & Fe^{+3} are:

Sol. $Fe^{+2} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^6 = 4$ unpaired e^-

$Fe^{+3} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5 = 5$ unpaired e^-

Concept Application

30. How many unpaired electrons are there in Ni^{+2} ion if the atomic number of Ni is 28?

[✓ (a) 2] (b) 3

(c) 4 (d) 1

31. Which of the following sets of quantum numbers are impossible for electrons ?

Set	n	ℓ	m	s
(i)	1	0	1	$+\frac{1}{2}$
(ii)	3	0	0	$-\frac{1}{2}$
(iii)	1	2	2	$+\frac{1}{2}$
(iv)	4	3	–3	$+\frac{1}{2}$
(v)	5	2	1	$-\frac{1}{2}$
(vi)	3	2	1	0

(a) (i), (iii)

(b) (i), (ii), and (vi)

[✓ (c) (i), (iii), and (vi)]

(d) (i), (iii), and (iv)

32. The total magnitude of spin resulting from a d^7 configuration is:

(a) 1 (b) 2

(c) $\frac{5}{2}$ [✓ (d) $\frac{3}{2}$]

H/W

33. Given is the electronic configuration of element X:

K L M N

2 8 11 2

The number of electrons present with $\ell = 2$ in an atom of element X is:

[✓ (a) 3] (b) 6

(c) 5 (d) 4

Aarambh (Solved Examples)

1. The ionization energy of H-atom is 13.6 eV. The ionization energy of Li^{+2} ion will be:

(*a*) 13.6 eV (*b*) 27.2 eV (*c*) 54.4 eV (*d*) 122.4 eV

Sol. E_1 for $Li^{+2} = E_1$ for $H \times Z^2$ [for Li, Z = 3]

$= 13.6 \times 9 = 122.4$ eV

Therefore, option (*d*) is the correct answer.

2. Which of the following pairs have same specific charge $\left(\frac{e}{m}\right)$?

(*a*) Electron & Proton (*b*) Electron & Positron

(*c*) Proton & Deuteron (*d*) Proton & Positron

Sol. Positron is antiparticle of e.

Therefore, option (*b*) is the correct answer.

3. Wavelength of photon which have energy equal to average of energy of photons with $\lambda_1 = 4000$ Å and $\lambda_2 = 6000$ Å will be:

(*a*) 5000 Å (*b*) 4800 Å (*c*) 9600 Å (*d*) 2400 Å

Sol. According to question $E = \frac{E_1 + E_2}{2}$

$$\text{or } \frac{hc}{\lambda} = \frac{\frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}}{2}$$

$$\text{or } \frac{1}{\lambda} = \left(\frac{\frac{1}{4000} + \frac{1}{6000}}{2}\right)$$

or $\lambda = 4800$ Å

Therefore, option (*b*) is the correct answer.

4. The force of attraction on electron by the nucleus is directly proportional to

(*a*) $\frac{n^3}{Z^4}$ (*b*) $\frac{Z^3}{n^4}$ (*c*) $\frac{n^4}{Z^2}$ (*d*) $\frac{Z^2}{n^4}$

Sol. $F = \frac{q_1 q_2}{r^2}$ ...(i)

$q_1 = e^-, q_2 = ze^-$

and $r = 0.529 \frac{n^2}{Z}$ Å

Putting all these values in equation (i)

$$F = \frac{Ke^2 Z}{\left(0.529 \frac{n^2}{Z} \text{Å}\right)^2} \text{ or } F \propto \frac{Z^3}{n^4}$$

Therefore, option (*b*) is the correct answer.

5. Rydberg give the equation for all visible radiation in the hydrogen spectrum as $\lambda = \frac{kn^2}{n^2 - 4}$. The value of *k* in terms of Rydberg constant is:

(*a*) $4R$ (*b*) $\frac{R}{4}$ (*c*) $\frac{4}{R}$ (*d*) R

Sol. According to question

$z = 1, n_1 = 2, n_2 = n$

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right](z)^2$$

$$\text{or } \frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n^2}\right](1)^2$$

$$\text{or } \frac{1}{\lambda} = R_H \left[\frac{n^2 - 4}{4n^2}\right]$$

$$\text{or } \lambda = \frac{4n^2}{R_H(n^2 - 4)} \quad \text{... (i)}$$

$$\text{And also } \lambda = \frac{kn^2}{(n^2 - 4)} \text{ (given)} \quad \text{... (ii)}$$

From (i) and (ii)

$$k = \frac{4}{R_H}$$

Therefore, option (*c*) is the correct answer.

6. The orbital angular momentum of an electron is $\sqrt{3}\frac{h}{\pi}$. Which of the following may be the permissible value of angular momentum of this electron revolving in unknown Bohr orbit?

(*a*) $\frac{h}{\pi}$ (*b*) $\frac{h}{2\pi}$ (*c*) $\frac{3h}{2\pi}$ (*d*) $\frac{2h}{\pi}$

Sol. Orbital angular momentum $= \sqrt{l(l+1)}\frac{h}{2\pi}$

Orbital angular momentum $= \sqrt{3}\frac{h}{\pi}$

$$\therefore \sqrt{l(l+1)} \times \frac{h}{2\pi} = \sqrt{3}\frac{h}{\pi}$$

On Solving above equation, we get $l = -4$ and 3 (-4 not allowed as $l < 0$)

For $l = 3$, n = 4, 5, 6 (Possible)

Therefor possible angular momentum

$$= \frac{4h}{2\pi}, \frac{5h}{2\pi}, \frac{6h}{2\pi}, \frac{7h}{2\pi}, ...$$

Therefore, option (*d*) is the correct answer.

7. The bond dissociation energy of Cl–Cl bond in chlorine gas is 240 kJ/mol. Calculate the longest wavelength (in nm) of EMR needed to dissociate bond. Assume one photon may dissociate only one bond.

Sol. $E = \frac{240 \times 10^3}{6 \times 10^{23}} = \frac{1 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda} = \lambda = 496$ nm

Therefore, [496] is the correct answer.

8. A sample of He^+ ions in ground state absorbs the radiation of xÅ. Subsequently, the sample emit radiation of 6 different wavelength. Calculate the value of x.

Sol. $\frac{(n_2-n_1)(n_2-n_1+1)}{2}=6$ given, $n_1=1$

$\frac{(n-1)(n-1+1)}{2}=6$

On solving

$n=4$ or $n=3$

6 different wavelength will be obtained only from $n=4$

$\frac{1}{x}=R_H\times z^2\left(\frac{1}{1^2}-\frac{1}{4^2}\right)\Rightarrow\frac{1}{x}=R_H\times z^2\left(\frac{1}{1}-\frac{1}{16}\right)$

$\frac{1}{x}=R_H\times\frac{\cancel{4}\times15}{\cancel{16}\ 4}$

or $n=\frac{4}{15R_H}$ or $n=\frac{4}{15\times1.09678\times10^7\,m^{-1}}$

or $n=243$ Å

Therefore, [243] is the correct answer.

9. Through what potential difference an α-particle should be accelerated to have speed 5×10^6 m/s.

Sol. $qV=\frac{1}{2}mv^2$

$(2\times1.6\times10^{-19}\times V)=\frac{1}{2}\times4\times1.66\times10^{-27}\times(5\times10^6)^2$

$V=0.26$ MV

Therefore, [0.26] is the correct answer.

10. Calculate the energy per quanta (in terms of 10^{-25}) of an EMR of frequency 400 MHz.

Sol. $E=nh\nu$ or $\frac{E}{n}=6.626\times10^{-34}\times400\times10^6$ J/quanta

or $\frac{E}{n}=2.65\times10^{-25}$ J/quanta

Therefore, [2.65] is the correct answer.

11. Calculate the wavelength (in Å) of an EMR of energy 3.1eV/quanta.

Sol. $\frac{E}{n}=h\frac{c}{\lambda}\Rightarrow3.1\times1.602\times10^{-19}=\frac{1\times6.62\times10^{-34}\times3\times10^8}{\lambda}$

or $\lambda=4002.6$Å

Therefore, [4002.6] is the correct answer.

12. The energy level of a hypothetical atom for 1st, 2nd and 3rd levels are E, 4E, 2E respectively. If photon of wavelength is λ emitted for a transition 3 to 1. Calculate the wavelength for transition 2 to 1 in terms of λ.

Sol. Energy of photon released = E_3-E_1 ...(i)

As we know that energy of photon is given by $=\frac{hc}{\lambda}$

where λ wavelength of photon

from (i)

$\frac{hc}{\lambda}=E_3-E_1=E\Rightarrow\lambda=\frac{hc}{E}$ ... (ii)

On transition from 2 → 1 energy level.

Energy of photon released = E_2-E_1 ... (iii)

Let, wavelength of photon released be λ'

⇒ Energy of photon released = $\frac{hc}{\lambda'}$

From (iii)

$E_2-E_1=\frac{hc}{\lambda'}\Rightarrow3E=\frac{hc}{\lambda'}\Rightarrow\lambda'=\frac{hc}{3E}=\frac{1}{3}\left(\frac{hc}{E}\right)$

$\Rightarrow\lambda'=\frac{1}{3}(\lambda)$(from (ii)) $\Rightarrow\lambda'=\frac{\lambda}{3}$

Therefore, wavelength of photon emitted for transition 2 → 1 is $\frac{\lambda}{3}$.

13. Arrange the particle in their increasing order of specific charge ratio.

$Na^+, Li^+, F^-, Mg^{2+}, Al^{3+}$

Sol. $Na^+=\frac{1}{23};Li^+=\frac{1}{7};F^-=\frac{1}{19};Mg^{2+}=\frac{2}{24}=\frac{1}{12};Al^{3+}=\frac{3}{27}=\frac{1}{9}$

Therefore, correct order is $Na^+<F^-<Mg^{2+}<Al^{3+}<Li^+$.

14. If the P.E. of an electron is –6.8 eV in hydrogen atom then find

(*a*) K.E. (*b*) E

(*c*) No. of orbit (*c*) Radius of orbit.

Sol. (*a*) P.E. = –2K.E.

$-6.8=-2$K.E.

$\frac{6.8}{2}=$ K.E. ⇒ K.E. = 3.4eV

(*b*) E = –K.E.

= –3.4 eV

(*c*) Orbit = 2nd

$\because E=-13.6\times\frac{Z^2}{n^2}$

$\therefore-3.4=-13.6\times\frac{1^2}{n^2}$

$\Rightarrow n^2=\frac{-13.6}{-3.4}=4$

i.e. $n=2$

(*d*) $r=0.529\times\frac{n^2}{Z}$ Å

$r=0.529\times\frac{(2)^2}{1}$ Å

$=0.529\times4$Å $=2.12$Å

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. In lithium nitride, the nitride ion is composed of:
   (*a*) 7 – protons + 10 electrons
   (*b*) 12 – protons + 5 electrons
   (*c*) 12 – protons + 8 electrons
   (*d*) 10 – protons + 7 electrons

2. The wavelength of an emission line obtained for Li^{2+} during a electronic transition from $n_2 = 2$ to $n_1 = 1$ is: (R = Rydberg constant)
   (*a*) 3R/4 (*b*) 27R/4
   (*c*) 4/3R (*d*) 4/27R

3. A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.
   (*a*) $20.12 \times 10^{20}\ s^{-1}$ (*b*) $2.012 \times 10^{20}\ s^{-1}$
   (*c*) $4.969 \times 10^{-19}\ s^{-1}$ (*d*) $49.69 \times 10^{-19}\ s^{-1}$

4. The radius of the first orbit of hydrogen atom is 0.52×10^{-8} cm. The radius of the first orbit of He^+ ion is
   (*a*) 0.26×10^{-8} cm (*b*) 0.52×10^{-8} cm
   (*c*) 1.04×10^{-8} cm (*d*) 2.08×10^{-8} cm

5. The de-Broglie wavelength associated with particle of mass 10^{-6} kg moving with a velocity of 10 m/sec is:
   (*a*) 6.63×10^{-7} m (*b*) 6.63×10^{-16} m
   (*c*) 6.63×10^{-21} m (*d*) 6.63×10^{-29} m

H.W 6. The set of quantum no. not applicable for an electron-
   (*a*) $2, 0, 0, -\frac{1}{2}$ [✓ (*b*) $3, 1, -2, +\frac{1}{2}$]
   (*c*) $4, 2, -2, -\frac{1}{2}$ (*d*) $6, 0, 0, +\frac{1}{2}$

7. The atomic numbers of elements X, Y and Z are 19, 21 and 25 respectively. The number of electrons present in the M shells of these elements follow the order.
   (*a*) Z > X > Y (*b*) X > Y > Z
   (*c*) Z > Y > X (*d*) Y > Z > X

8. Light of wavelength λ shines on a metal surface with intensity X and the metal emits Y electrons per second of average energy, Z. What will happen to Y and Z if x is doubled?
   (*a*) Y will be double and Z will become half
   (*b*) Y will remain same and Z will be doubled
   (*c*) Both Y and Z will be doubled
   (*d*) Y will be doubled but Z will remain same

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.

(*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.

(*c*) Assertion is True but the Reason is False.

(*d*) Assertion is False but Reason is True.

9. **Assertion:** It is impossible to determine the exact position and exact momentum of an electron simultaneously.

   Reason: The path of an electron in an atom is clearly defined.

10. **Assertion:** In $3d_{z^2}$, the number of radial nodes is zero.

   Reason: No. of radial nodes of atomic orbitals is equal to value of $(n - \ell - 1)$.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the following rules with their statements:

	Column-I		Column-II
A.	Hund's Rule	p.	No two electrons in an atom can have the same set of four quantum numbers.
B.	Aufbau Principle	q.	Half-filled and completely filled orbitals have extra stability
C.	Pauli Exclusion Principle	r.	Pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital is singly occupied.
D.	Heisenberg's Uncertainty principle	s.	It is impossible to determine the exact position and exact momentum of a subatomic particle simultaneously.
		t.	In the ground state of atoms, orbitals are filled in the order of their increasing energies.

   (*a*) A-(s); B-(r); C-(p); D-(q)
   (*b*) A-(s); B-(p); C-(q); D-(t)
   (*c*) A-(r); B-(q); C-(s); D-(p)
   (*d*) A-(r); B-(t); C-(p); D-(s)

12. Match the following

	Column-I		Column-II
A.	X-rays	p.	$v = 10^0 - 10^4$ Hz
B.	UV	q.	$v = 10^{11} - 10^{13}$ Hz
C.	Long radio waves	r.	$v = 10^{16}$ Hz
D.	Microwave	s.	$v = 10^{18}$ Hz

   (*a*) A-(s); B-(r); C-(p); D-(q)
   (*b*) A-(q); B-(s); C-(p); D-(r)
   (*c*) A-(r); B-(q); C-(s); D-(p)
   (*d*) A-(s); B-(p); C-(q); D-(r)

SHORT ANSWER TYPE QUESTIONS

13. Calculate the wave number and frequency of yellow radiation having wavelength 3200 Angstrom.

14. For a metal, threshold frequency is $6.8 \times 10^{14}\ s^{-1}$. Calculate the kinetic energy of an electron when frequency $1.0 \times 10^{15}\ s^{-1}$ hits the metal.

15. If an electron in a hydrogen atom is in the $n = 4$ energy level and undergoes transition to the $n = 2$ energy level, calculate the energy change and the frequency of the emitted photon using Bohr's model.

16. Calculate the lowest energy of the spectral lines emitted by the hydrogen atom in the Lyman series.

17. Calculate the minimum uncertainty in the position of a particle if its uncertainty in momentum is 2.0×10^{-27} kg·m/s

18. Calculate the number of electrons in atom having following quantum numbers:

(*a*) $n = 2, m_s = -1/2$

(*b*) $n = 4, l = 0$

LONG ANSWER TYPE QUESTIONS

19. Explain the Pauli Exclusion Principle and Hund's Rule. How do these principles affect the filling of electron energy levels and sublevels in atoms?

20. (*a*) Calculate the velocity of the electron in the first Bohr orbit having radius a_0. Also, calculate the de-Broglie wavelength in m.

(*b*) Electromagnetic radiation having a wavelength 340 nm is just sufficient to cause ionization of sodium atoms. calculate the ionization energy in kJ/mol.

21. On passing electric discharge through hydrogen gas, the hydrogen molecules undergo dissociation and produce excited hydrogen atoms. These excited atoms emit electromagnetic radiations with discrete frequencies having formula:

$$\bar{v} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

What points of Bohr model can be used to reach this formula? Based on these points, derive the formula and explain each step along with each term.

22. Describe the significance of quantum numbers (n, l, m_l, and m_s) in the quantum mechanical model of the atom. Explain how these quantum numbers define electronic states within an atom.

23. A photon has wavelength 4×10^{-7} strikes on a metal surface where the work function is 1.23 eV. Determine the

(*a*) energy of the photon in eV

(*b*) the kinetic energy of the emission

(*c*) velocity of the photoelectron

CASE STUDY BASED QUESTIONS

24. In 1909, Ernest Rutherford conducted a ground breaking experiment known as the "Rutherford gold foil experiment" to investigate the structure of the atom. At that time, J.J. Thomson's "plum pudding" model was widely accepted, suggesting that atoms were composed of a positively charged "pudding" with negatively charged electrons embedded within it. Rutherford's experiment aimed to test this model and explore the nature of atomic structure.

(*i*) What type of particles were used in Rutherford's gold foil experiment?

(*a*) Electrons (*b*) Neutrons

(*c*) Protons (*d*) Alpha particles

(*ii*) In the Rutherford gold foil experiment, most of the alpha particles:

(*a*) Passed through the gold foil without any deflection.

(*b*) Were completely absorbed by the gold foil.

(*c*) Were deflected at large angles.

(*d*) Were deflected at small angles.

(*iii*) What was the primary conclusion drawn from the Rutherford experiment?

(*a*) Atoms consist of a positively charged nucleus.

(*b*) Electrons are evenly distributed throughout the atom.

(*c*) Atoms are mostly empty space.

(*d*) Electrons are larger than protons.

(*iv*) How did Rutherford's findings impact the development of atomic theory?

(*a*) They confirmed the plum pudding model.

(*b*) They had no impact on atomic theory.

(*c*) They led to the development of the Bohr model.

(*d*) They supported the idea of continuous matter.

Prarambh (Topicwise)

DISCOVERY OF SUB ATOMIC PARTICLES, ATOMIC MODELS, NUCLEUS

1. The fraction of volume occupied by the nucleus with respect to the total volume of an atom is:

(*a*) 10^{-15} (*b*) 10^{-5}

(*c*) 10^{-30} (*d*) 10^{-10}

2. When lithium vapours were filled in the discharge tube for anode rays experiment, the anode rays were found to contain only Li^+ ions ($A = 7, Z = 3$). Therefore, each particle of anode rays contains

(*a*) 1 proton only.

(*b*) 3 protons and 4 neutrons only.

(*c*) 3 protons, 4 neutrons and 2 electrons.

(*d*) 3 protons, 3 neutrons and 3 electrons.

3. The ratio of e/m for a cathode ray:
   (a) Varies with a gas in a discharge tube.
   (b) Is fixed.
   (c) Varies with different electrodes.
   (d) Is maximum if hydrogen is taken.

4. Cathode rays have:
   (a) Mass only
   (b) Charge only
   (c) No mass and no charge
   (d) Mass and charge both

5. Which is the correct statement about proton?
   (a) It is a nucleus of deuterium.
   (b) It is an ionised hydrogen molecule.
   (c) It is an ionised hydrogen atom.
   (d) It is an α-particle.

6. Rutherford's experiment on scattering of α-particles showed for the first time that the atom has:
   (a) Electrons (b) Protons
   (c) Neutrons (d) Nucleus

7. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because:
   (a) Alpha particles are much heavier than electrons.
   (b) Alpha particles are positively charged.
   (c) Most part of the atom is empty space.
   (d) Alpha particles move with very high velocity.

8. 1 mole of diatomic gas A_2 contain 32 and 36 moles of electrons and neutrons respectively. The representation of the element is
   (a) $_{32}A^{68}$ (b) $_{16}A^{34}$
   (c) $_{16}A^{18}$ (d) $_{32}A^{36}$

9. Nucleons are:
   (a) Protons and neutrons.
   (b) Neutrons and electrons.
   (c) Protons and electrons.
   (d) Protons, neutrons and electrons.

10. The discovery of neutron came very late because:
   (a) It is present in nucleus.
   (b) It is a fundamental particle.
   (c) It does not move.
   (d) It does not carry any charge.

11. Atomic number of an element represents:
   (a) Number of neutrons in the nucleus.
   (b) Atomic mass of an element.
   (c) Valency of an element.
   (d) Number of protons in the nucleus.

12. The highest value of e/m of anode rays has been observed when the discharge tube is filled with:
   (a) Dinitrogen (b) Dioxygen
   (c) Dihydrogen (d) Helium

QUANTUM THEORY OF LIGHT & PHOTOELECTRIC EFFECT

13. The MRI (magnetic resonance imaging) body scanners used in hospitals operate with 400 MHz radio frequency. The wavelength corresponding to this radio frequency is:
   (a) 0.75 m (b) 0.75 cm
   (c) 1.5 m (d) 2 cm

14. Electromagnetic radiations of wavelength 242 nm is just sufficient to ionise Sodium atom. Then the ionisation energy of Sodium in kJ $mole^{-1}$ is:
   (a) 494.65 (b) 400
   (c) 247 (d) 600

15. A bulb of 40 W is producing a light of wavelength 620 nm with 80% of efficiency then the number of photons emitted by the bulb in 20 seconds are (1eV = 1.6×10^{-19} J, hc = 12400 eV Å):
   (a) 2×10^{18} (b) 10^{18}
   (c) 10^{21} (d) 2×10^{21}

16. Light of wavelength λ falls on metal having work function hc/λ_0. Photoelectric effect will take place only if :
   (a) $\lambda \geq \lambda_0$ (b) $\lambda \geq 2\lambda_0$
   (c) $\lambda \leq \lambda_0$ (d) $\lambda \leq \lambda_0/2$

17. A light whose frequency is equal to 6×10^{14} Hz is incident on a metal whose work function is 2 eV (h = 6.626×10^{-34} Js, 1 eV = 1.6×10^{-19} J). The maximum energy of electrons emitted will be:
   (a) 2.49 eV (b) 4.49 eV
   (c) 0.49 eV (d) 5.49 eV

18. A 600 W mercury lamp emits monochromatic radiation of wavelength 331.3 nm. How many photons are emitted from the lamp per second?
   (h = 6.626×10^{-34} Js, velocity of light = 3×10^8 ms^{-1})
   (a) 1×10^{19} (b) 1×10^{20}
   (c) 1×10^{21} (d) 1×10^{23}

19. Photoelectric effect can be explained by assuming that light:
   (a) Is a form of transverse wave.
   (b) Is a form of longitudinal wave.
   (c) Can be polarised.
   (d) Consists of quanta.

20. When the frequency of light incident on a metallic plate is doubled of threshold frequency, the K.E. of the emitted photoelectrons will be:
   (a) Doubled
   (b) Halved
   (c) Increased but more than double of the previous K.E.
   (d) Unchanged

21. A photon of 300 nm is absorbed by a gas and then emits two photons. One photon has a wavelength 496 nm then the wavelength of second photon is:
   (a) 759 (b) 857 (c) 957 (d) 657

BOHR MODEL

22. Which is the correct relationship:
(a) E_1 of H = 1/2 E_2 of He^+ = 1/3 E_3 of Li^{2+} = 1/4 E_4 of Be^{3+}
(b) $E_1(H) = E_2(He^+) = E_3(Li^{2+}) = E_4(Be^{3+})$
(c) $E_1(H) = 2E_2(He^+) = 3E_3(Li^{2+}) = 4E_4(Be^{3+})$
(d) No relation

23. If velocity of an electron in 1st orbit of H atom is V, what will be the velocity of electron in 3rd orbit of Li^{+2}?
(a) V (b) V/3
(c) 3 V (d) 9 V

24. In a certain electronic transition in the hydrogen atoms from an initial state (1) to a final state (2), the difference in the orbit radius $(r_1 - r_2)$ is 24 times the first Bohr radius. Identify the transition:
(a) 5 → 1 (b) 25 → 1
(c) 8 → 3 (d) 6 → 5

25. S_1 : Potential energy of the two opposite charge system increases with the decrease in distance.
S_2 : When an electron make transition from higher orbit to lower orbit, it's kinetic energy increases.
S_3 : When an electron make transition from lower energy to higher energy state its potential energy increases.
S_4 : 11eV photon can free an electron from the 1st excited state of He^+ -ion.
(a) T T T T (b) F T T F
(c) T F F T (d) F F F F

26. Energy of Bohr orbit:
(a) Increases as we move away from the nucleus.
(b) Decreases as we move away from the nucleus.
(c) Remains the same as we move away from the nucleus.
(d) None of the above.

27. The radius of the first orbit of H-atom is r. Then, the radius of the first orbit of Li^{2+} will be:
(a) r/9 (b) r/3
(c) 3r (d) 9r

28. According to Bohr theory, the angular momentum for an electron of 5th orbit is:
(a) 5 h/π (b) 2.5 h/π
(c) 5 π/h (d) 25 h/π

29. Which of the following electron transitions in hydrogen atom will require largest amount of energy?
(a) from n = 1 to n = 2
(b) from n = 2 to n = 3
(c) from n = ∞ to n = 1
(d) from n = 3 to n = 5

30. $E_n = -313.6/n^2$ kcal/mol. If the value of E = –34.84 kcal/mol, to which value does 'n' correspond?
(a) 4 (b) 3 (c) 2 (d) 1

31. Bohr's atomic model suggests that
(a) Electrons have a particles as well as wave character
(b) Atomic spectrum of atom should contain only five lines
(c) Electron on H-atom can have only certain values of angular momentum
(d) All of the above

32. In Bohr's model of the hydrogen atom, let r, v and E represent the orbit radius, speed of an electron and the total energy of the electron, respectively. Which of following relation is proportional to the orbit number n?
(a) v·r (b) r/E
(c) r/v (d) r·E

33. An electron in H-atom in its ground state absorbs 1.50 times as much as energy as the minimum required for its escape (13.6 eV) from the atom. Thus K.E. given to emitted electron is:
(a) 13.6 eV (b) 20.4 eV
(c) 34.0 eV (d) 6.8 eV

34. Bohr's theory is not valid for the species:
(a) H atom (b) He^+ ion
(c) Li^+ ion (d) Li^{2+} ion

35. If r_1 is the radius of the first orbit of hydrogen atom, then the radii of second, third and fourth orbitals in terms of r_1 are:
(a) r_1^2, r_1^3, r_1^4 (b) $8r_1, 27r_1, 64r_1$
(c) $4r_1, 9r_1, 16r_1$ (d) $2r_1, 6r_1, 8r_1$

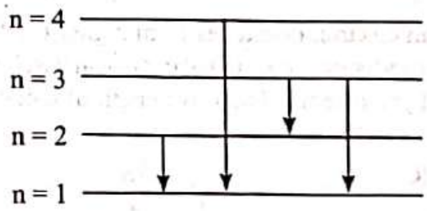
SPECTRUM

36. In a sample of H-atom electrons make transition from 5th excited state upto ground state, producing all possible types of photons, then number of lines in infrared region are:
(a) 4 (b) 5 (c) 6 (d) 3

37. Total no. of lines in Lyman series of H-spectrum will be (where n = no. of orbits):
(a) n (b) n – 1
(c) n – 2 (d) n (n + 1)

38. No. of visible lines when an electron returns from 5th orbit upto ground state in H-spectrum:
(a) 5 (b) 4
(c) 3 (d) 10

39. Suppose that a hypothetical atom gives a red, green, blue and violet line spectrum among given transition. Which jump according to figure would give off the red spectral line?



(a) 3 → 1 (b) 2 → 1
(c) 4 → 1 (d) 3 → 2

40. The difference between the wave number of 1st line of Balmer series and last line of Paschen series for Li^{2+} ion is:

(*a*) $\frac{R}{36}$ (*b*) $\frac{5R}{36}$ (*c*) 4R (*d*) $\frac{R}{4}$

41. The spectral lines corresponding to the radiation emitted by an electron jumping from higher orbits to first orbit belong to:

(*a*) Paschen series (*b*) Balmer series

(*c*) Lyman series (*d*) None of these

42. For the Paschen series, the value of n_1 and n_2 in the expression $\Delta E = R_H \times hc\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ is:

(*a*) $n_1 = 1, n_2 = 2, 3, 4...$ (*b*) $n_1 = 2, n_2 = 3, 4, 5...$

(*c*) $n_1 = 3, n_2 = 4, 5, 6...$ (*d*) $n_1 = 4, n_2 = 5, 6, 7...$

43. If the series limit of wavelength of the Lyman series for the hydrogen atoms is 912 Å, then the series limit of wavelength for the Balmer series of the hydrogen atom is:

(*a*) 912 Å (*b*) 912 × 2 Å

(*c*) 912 × 4 Å (*d*) 912/2 Å

44. The shortest λ for the Lyman series of hydrogen atom is ... (Given $R_H = 109678\ cm^{-1}$)

(*a*) 911.7 Å (*b*) 700 Å

(*c*) 600 Å (*d*) 811 Å

45. The frequency of first line of Balmer series in hydrogen atom is ν_0. The frequency of corresponding line emitted by singly ionised helium atom is:

(*a*) $2\nu_0$ (*b*) $4\nu_0$

(*c*) $\nu_0/2$ (*d*) $\nu_0/4$

46. Which of the following statement is not true?

(*a*) Lyman spectral series of hydrogen atom lies in the ultraviolet region of electromagnetic radiation.

(*b*) Balmer spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.

(*c*) Paschen spectral series of hydrogen atom lies in the visible region of electromagnetic radiation.

(*d*) Brackett spectral series of hydrogen atom lies in the infrared region of electromagnetic radiation.

47. The first emission line of Balmer series in H-spectrum has the wave number equal to:

(*a*) $\frac{9R_H}{400} cm^{-1}$ (*b*) $\frac{7R_H}{144} cm^{-1}$

(*c*) $\frac{3R_H}{4} cm^{-1}$ (*d*) $\frac{5R_H}{36} cm^{-1}$

48. When an electron de-excites from higher orbit in H-atom, only two radiations are emitted out one in Paschen series and one in Lyman series. The wavelength of radiation emitted out in Lyman series is:

(*a*) $\frac{8R}{9}$ (*b*) $\frac{3R}{4}$

(*c*) $\frac{4}{3R}$ (*d*) $\frac{9}{8R}$

DE-BROGLIE WAVELENGTH AND HEISENBERG UNCERTAINITY PRINCIPLE

49. The momentum of a photon of wavelength 6626 nm will be

(*a*) 10^{-28} kg ms^{-1} (*b*) 10^{-25} kg ms^{-1}

(*c*) 10^{-31} kg ms^{-1} (*d*) Zero

50. De-Broglie wavelength of electron in second orbit of Li^{2+} ion will be equal to de-Broglie wavelength of electron in:

(*a*) n = 3 of H-atom (*b*) n = 4 of C^{5+} ion

(*c*) n = 6 of Be^{3+} ion (*d*) n = 3 of He^{+} ion

51. de-Broglie equation describes the relationship of wavelength associated with the motion of an electron and its:

(*a*) Mass (*b*) Energy

(*c*) Momentum (*d*) Charge

52. A body of mass 'x' kg is moving with velocity of 100 m sec^{-1}. It's de-Broglie wavelength is 6.62×10^{-35} m. Hence 'x' is ($h = 6.62 \times 10^{-34}$ J sec):

(*a*) 0.25 kg (*b*) 0.15 kg

(*c*) 0.2 kg (*d*) 0.1 kg

53. The wavelengths of electron waves in two orbits is 3 : 5. The ratio of kinetic energy of electrons will be:

(*a*) 25 : 9 (*b*) 5 : 3 (*c*) 9 : 25 (*d*) 3 : 5

54. A ball of mass 200 g is moving with a velocity of 10 m sec^{-1}. If the error in measurement of velocity is 0.1%, the uncertainty in its position is:

(*a*) 3.3×10^{-31} m (*b*) 3.3×10^{-27} m

(*c*) 5.3×10^{-25} m (*d*) 2.64×10^{-32} m

55. If the radius of first Bohr orbit is x, then de-Broglie wavelength of electron in 3rd orbit is nearly:

(*a*) 2πx (*b*) 6πx (*c*) 9x (*d*) x/3

56. Which of the following particles moving with same velocity would be associated with smallest de-Broglie wavelength?

(*a*) Dihydrogen molecule (*b*) Dioxygen molecule

(*c*) Helium molecule (*d*) Dinitrogen molecule

QUANTUM NUMBERS & ELECTRONIC CONFIGURATION

57. Spin magnetic moment of X^{n+} (Z = 26) is $\sqrt{24}$ B.M. Hence number of unpaired electrons and value of n respectively are:

(*a*) 4, 2 (*b*) 2, 4 (*c*) 3, 1 (*d*) 0, 2

58. Which of the following ions has the maximum number of unpaired d-electrons?

(*a*) Zn^{2+} (*b*) Mn^{2+} (*c*) Ni^{3+} (*d*) Cu^{+}

59. Consider the ground state of Cr atom (Z = 24). The numbers of electrons with the azimuthal quantum numbers, $\ell = 1$ and 2 are, respectively:

(*a*) 16 and 5 (*b*) 12 and 5

(*c*) 16 and 4 (*d*) 12 and 4

HW **60.** The orbital angular momentum of an electron in 2s-orbital is:

(a) $+\frac{1}{2}\frac{h}{2\pi}$ [✓ (b) Zero]

(c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\frac{h}{2\pi}$

61. The possible value of ℓ and m for the last electron in the Cl^- ion are:

(a) 1 and 2 (b) 2 and + 1

(c) 3 and –1 (d) 1 and –1

62. For an electron, subshell with n = 3 has only one radial node. The orbital angular momentum of the electron will be:

(a) 0 (b) $\sqrt{6}\frac{h}{2\pi}$

(c) $\sqrt{2}\frac{h}{2\pi}$ (d) $3\left(\frac{h}{2\pi}\right)$

QUANTUM MECHANICAL MODEL OF ATOM, SCHRODINGER WAVE EQUATION AND ORBITAL CONCEPT

63. The maximum radial probability in 1s-orbital occurs at a distance when: [r_0 = Bohr radius]

(a) $r = r_0$ (b) $r = 2r_0$

(c) $r = \frac{r_0}{2}$ (d) $2r = \frac{r_0}{2}$

64. The maximum probability of finding an electron in the d_{xy} orbital is :

(a) Along the x-axis.

(b) Along the y-axis.

(c) At an angle of 45° from the x and y axis.

(d) At an angle of 90° from the x and y axis.

65. $3p_y$ orbital has..........nodal plane :

(a) XY (b) YZ

(c) ZX (d) All of these

66. A 3p-orbital has:

(a) Two non-spherical nodes.

(b) Two spherical nodes.

(c) One spherical and one non spherical nodes.

(d) One spherical and two non spherical nodes.

67. According to Schrodinger model nature of electron in an atom is as:

(a) Particle only.

(b) Wave only.

(c) Particle and wave nature simultaneous.

(d) Sometimes waves and sometimes particle.

68. Consider the following statements:

(A) Electron density in the XY plane in $3d_{x^2-y^2}$ orbital is zero.

(B) Electron density in the XY plane in $3d_{z^2}$ orbital is zero.

(C) 2s orbital has one spherical nodal.

(D) For $2p_z$ orbital, XY is the nodal plane.

Which of these are incorrect statements?

(a) A & C (b) D & C

(c) Only B (d) A & B

69. Which of the following d-orbitals has dough-nut shape ?

(a) d_{xy} (b) d_{yz}

(c) $d_{x^2-y^2}$ (d) d_{z^2}

70. The permissible solution to the Schrodinger wave equation gave an idea of only .... quantum numbers.

(a) 4 (b) 3

(c) 2 (d) 1

Prabal (JEE Main Level)

1. A light source of wavelength (λ) illuminates a metal and ejects photo-electrons with $(K.E.)_{max}$ = 1 eV.

Another light source of wavelength λ/3, ejects photo-electrons from same metal with $(K.E.)_{max}$ = 5eV.

Find the value of work function?

(a) 1 eV (b) 2 eV

(c) 0.5 eV (d) None of these

2. A single electron species in energy level (orbit number n) with energy X was provided with excess of energy so that it jumps to higher energy level with energy Y. If it can emit radiations of six different wavelengths on de-excitement between these two energy levels, then the correct relation is

(a) $\frac{X}{Y} = (n-1)^2$ (b) $\frac{X}{Y} = 1 + \frac{3}{n}$

(c) $\sqrt{\frac{X}{Y}} = 1 + \frac{3}{n}$ (d) $\frac{X}{Y} = 1 + \frac{n}{3}$

3. The potential energy of the electron present in the ground state of Be^{3+} ion is represented by:

(a) $+\frac{e^2}{\pi \epsilon_0 r}$ (b) $-\frac{e}{\pi \epsilon_0 r}$

(c) $-\frac{e^2}{\pi \epsilon_0 r^2}$ (d) $-\frac{e^2}{\pi \epsilon_0 r}$

4. Which transition in Li^{2+} would have the same wavelength as the 2 → 4 transition in He^+ ion?

(a) 4 → 2 (b) 1 → 2

(c) 3 → 6 (d) 6 → 2

5. Let υ_1 be the frequency of the series limit of the Lyman series, υ_2 be the frequency of the first line of the Lyman series, and υ_3 be the frequency of the series limit of the Balmer series:

(*a*) $\upsilon_1 - \upsilon_2 = \upsilon_3$

(*b*) $\upsilon_2 - \upsilon_1 = \upsilon_3$

(*c*) $\upsilon_3 = 1/2\,(\upsilon_1 - \upsilon_3)$

(*d*) $\upsilon_1 + \upsilon_2 = \upsilon_3$

6. In a sample of H-atoms, electrons de-excite from a level 'n' to 1. The total number of lines belonging to Balmer series are two. If the electrons are ionised from level 'n' by photons of energy 13 eV. Then the kinetic energy of the ejected photoelectrons will be :

(*a*) 12.15 eV (*b*) 11.49 eV

(*c*) 12.46 eV (*d*) 12.63 eV

7. A particle X moving with a certain velocity has a de-Broglie wave length of 1Å. If particle Y has a mass of 25% that of X and velocity 75% that of X, de-Broglie wave length of Y will be:

(*a*) 3 Å (*b*) 5.33 Å

(*c*) 6.88 Å (*d*) 48 Å

8. The ratio of the de-Broglie wavelength of a proton and α-particles will be 1 : 2 if their:

(*a*) Velocity are in the ratio 1 : 8.

(*b*) Velocity are in the ratio 8 : 1.

(*c*) Kinetic energy are in the ratio 1 : 64.

(*d*) Kinetic energy are in the ratio 1 : 256.

9. Consider an electron in the nth orbit of a hydrogen atom in the Bohr model. The circumference of the orbit can be expressed in terms of the de-Broglie wavelength (λ) of the electron as:

(*a*) (0.529) nλ (*b*) $\sqrt{n}\lambda$

(*c*) (13.6) λ (*d*) nλ

H.W **10.** In case of $d_{x^2-y^2}$ orbital:

(*a*) Probability of finding the electron along x-axis is zero.

(*b*) Probability of finding the electron along y-axis is zero.

[✓ (*c*)] Probability of finding the electron is maximum along x and y-axis.

(*d*) Probability of finding the electron is zero in x-y plane.

H.W **11.** The value of the spin magnetic moment of a particular ion is 2.83 Bohr magneton. The ion is:

(*a*) Fe^{2+} [✓ (*b*)] Ni^{2+} (*c*) Mn^{2+} (*d*) Co^{3+}

H.W **12.** If n and ℓ are respectively the principal and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any orbit is:

(*a*) $\sum_{\ell=1}^{\ell=n} 2(2\ell+1)$ (*b*) $\sum_{\ell=1}^{\ell=n-1} 2(2\ell+1)$

(*c*) $\sum_{\ell=0}^{\ell=n+1} 2(2\ell+1)$ [✓ (*d*)] $\sum_{\ell=0}^{\ell=n-1} 2(2\ell+1)$

13. The difference in Bohr's radius of H atom for (n + 1) and nth radius is equal to (n – 1)th Bohr radius. The value of n is:

(*a*) 3 (*b*) 2 (*c*) 4 (*d*) 5

14. An electron, a proton and an alpha particle have kinetic energies of 16E, 4E and E respectively. What is the qualitative order of their de-Broglie wavelengths?

(*a*) $\lambda_e > \lambda_p = \lambda_\alpha$ (*b*) $\lambda_p = \lambda_\alpha > \lambda_e$

(*c*) $\lambda_p > \lambda_e > \lambda_\alpha$ (*d*) $\lambda_\alpha > \lambda_e >> \lambda_p$

15. In an atom, two electrons move around the nucleus in circular orbits of radii R and 4R respectively. The ratio of the time taken by them to complete one revolution is:

(*a*) 1 : 4 (*b*) 4 : 1

(*c*) 1 : 8 (*d*) 8 : 7

16. An electron is continuously accelerated in vacuum tube under applied potential difference. Calculate the change in kinetic energy if de-Broglie wavelength is decreased by 2%

(*a*) 1% (*b*) 2%

(*c*) 3% (*d*) 4%

17. The difference in angular momentum associated with the electron in two successive orbits of hydrogen atom is:

(*a*) h/π (*b*) h/2π

(*c*) h/2 (*d*) (n – 1) h/2π

18. An α–particle is accelerated from rest through a potential difference of 6.0 V. It's de-Broglie wavelength is:

(*a*) 5 Å (*b*) 4.13 pm

(*c*) 414.6 Å (*d*) 5 nm

19. A photon of 2.55 eV is emitted out by an electronic transition in hydrogen atom. The change in de-Broglie wavelength of the electron is:

(*a*) 3.32 Å (*b*) 4.13 Å

(*c*) 6.64 Å (*d*) 9.96 Å

H.W **20.** An electron that has the quantum numbers n = 3 and m = 2:

(*a*) Must have l = 3, 4 or 5

(*b*) Must have l = 2, 3 or 4

(*c*) Must have l = 0, 1 or 2

[✓ (*d*)] Must have l = 2

H.W **21.** Electronic configuration of an element is $1s^2, 2s^1, 2p^2$. It is:

(*a*) Ground state configuration of B (Z = 5).

(*b*) Excited state configuration of B.

(*c*) Ground state configuration of C^+ ion (Z = 6).

(*d*) Impossible configuration.

22. What is the most probable distance of a 1s-electron in a He^+ ion? The wave function for 1s-orbital is given by

$\psi = \sqrt{\left(\frac{Z^3}{\pi a_0^3}\right)}e^{-Zr/a_0}$, where a_0 = radius of first Bohr's orbit in H-atom = 52.9 pm.

(*a*) 52.9 pm (*b*) 13.25 pm

(*c*) 6.61 pm (*d*) 26.45 pm

23. The dissociation energy of H_2 is 429.0 kJ/mol. If H_2 is dissociated by illumination with radiation of wavelength 270.0 nm, then what percentage of radiant energy will be converted into kinetic energy? ($h = 6.6 \times 10^{-34}$ Js, $N_A = 6 \times 10^{23}$)

(*a*) 1.25% (*b*) 3.26%

(*c*) 2.46% (*d*) 7.5%

H.W **24.** The magnitude of the orbital angular momentum of an electron is given by $L = \sqrt{5}\ h/\pi$. How many orbitals of this kind are possible, belonging to an orbit?

(*a*) 4 (*b*) 5 (*c*) 11 (*d*) 9

H.W **25.** How many electrons can fit into the orbitals that comprise the 3rd quantum shell, n = 3?

(*a*) 2 (*b*) 8 [✓ (*c*) 18] (*d*) 32

HW **26.** Which of the following sets of quantum numbers is correct for an electron in 4f-orbital?

(*a*) $n = 4, l = 3, m = +4; s = +1/2$

(*b*) $n = 4, l = 4, m = -4, s = -1/2$

[✓ (*c*) $n = 4, l = 3, m = +1, s = +1/2$]

(*d*) $n = 3, l = 2, m = -2, s = +1/2$

H.W **27.** In any subshell, the maximum number of electrons having same values of spin quantum number is:

(*a*) $\sqrt{l(\ell+1)}$ (*b*) $l + 2$

[✓ (*c*) $2l + 1$] (*d*) $4l + 2$

H.W **28.** Total number of values of "m" for n = 4 is:

(*a*) 8 [✓ (*b*) 16]

(*c*) 12 (*d*) 20

H.W **29.** The electronic configuration of an atom/ion can be defined by which of the following?

(*a*) Aufbau principle.

(*b*) Pauli's exclusion principle.

(*c*) Hund's rule of maximum multiplicity.

[✓ (*d*) All of these.]

H.W **30.** An ion which has 18 electrons in the outermost shell is:

(*a*) K^+ [✓ (*b*) Cu^+]

(*c*) Cs^+ (*d*) Th^{4+}

31. A strong argument for the charge and particle nature of cathode rays is:

(*a*) They can rotate paddle wheel.

(*b*) They can propagate in vacuum.

(*c*) They cast shadows.

(*d*) They are deflected by electric and magnetic fields.

H.W **32.** The ratio of angular momentum in 3rd orbit and orbital angular momentum of 3d-orbital is:

(*a*) $\sqrt{6}$ [✓ (*b*) $\sqrt{\frac{3}{2}}$]

(*c*) $\sqrt{\frac{2}{3}}$ (*d*) $\frac{1}{\sqrt{6}}$

H.W **33.** Which of the following statements is not correct?

(*a*) The shape of an atomic orbital depends on the azimuthal quantum number.

(*b*) The orientation of an atomic orbital depends on the magnetic quantum number.

(*c*) The energy of an electron in an atomic orbital of multi-electron atom depends only on the principal quantum number.

(*d*) All of these

34. Gases begin to conduct electricity in discharge tube at low pressure because:

(*a*) At low pressures, gases turn to plasma.

(*b*) Colliding electrons can acquire higher kinetic energy due to increased mean free path leading to ionisation of atoms.

(*c*) Atoms break up into electrons and protons.

(*d*) The electrons in atoms can move freely at low pressure.

35. The uncertainty in momentum of an electron is 1×10^{-5} kg ms^{-1}. The uncertainty in its position will be ($h = 6.626 \times 10^{-34}$ J.s):

(*a*) 1.05×10^{-28} m (*b*) 1.05×10^{-26} m

(*c*) 5.27×10^{-30} m (*d*) 5.25×10^{-28} m

INTEGER TYPE QUESTIONS

36. Number of possible spectral lines which may be emitted in Bracket series in H atom if electrons present in 9th excited level returns to ground level, are ________.

37. Electrons in a sample of H-atoms make transitions from state n = x to some lower excited state. The emission spectrum from the sample is found to contain only the lines belonging to a particular series. If one of the photons had an energy of 0.6375 eV. Then find the value of x.

[Take 0.6375 eV = 3/4 × 0.85 eV]

38. Magnetic moment of X^{3+} ion of 3d series is $\sqrt{35}$ BM. What is atomic number of X^{3+}?

39. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ(eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

40. Photons of same energy were allowed to strike on two different samples of hydrogen atoms, one having each atom in ground state and other in a particular excited state of orbit number n. The photonic beams ionize the hydrogen atoms in both the samples. If the difference in maximum kinetic energy of emitted photoelectron from both the samples is 12.75 eV, then find the value of n.

41. A photon having $\lambda = 960$ Å causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in kJ.

(Use : hc = 1240 eV × nm and $1\frac{eV}{atom} = 96.0$ kJ/mol.)

42. The work function for a metal is 40 eV. To emit photo electrons of zero velocity from the surface of the metal the wavelength of incident light should be x nm. Find value of x.

43. If first ionization potential of a hypothetical atom is 16 V, then the first excitation potential [in eV] will be:

44. Electrons in the H-atoms jump from some higher level upto 3^{rd} energy level. If three spectral lines are possible for the transition, find the initial orbit of electron.

45. In H-spectrum, longest wavelength of Lyman series is 120 nm and shortest wavelength of Balmer series is 360 nm. From this data, find longest wavelength [in nm] of photon, that can ionize this H-atom.

46. The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the (n = 4)state. Calculate the wavelength (in nm) of the photon.

47. When a certain metal was irradiated with light of frequency $4.0 \times 10^{16}\ s^{-1}$, the photoelectrons emitted had three times the kinetic energy as the kinetic energy of photoelectrons emitted with the metal was irradiated with light of frequency $2.0 \times 10^{16}\ s^{-1}$. Calculate the critical frequency (v_0 in $10^{16}\ s^{-1}$) of the metal.

48. An electron in He^+ ion occupies ground state. It is excited to next higher state. The ratio of circumference of excited to ground state is ______.

49. H-like species emitted a photon corresponding to the first line of Lyman series. The photon liberated a photoelectron from He^+ in ground state. The de-Broglie wavelength of the photoelectron is 2 Å. Calculate the atomic number of H-like species.

50. In a sample of hydrogen atoms, electrons jump from 10th excited state to ground state. If x are the number of different ultraviolet radiations, y are number of different visible radiations and z are number of different infrared radiations. Find the value of z – (x + y).

[Assume all the Balmer lines lie within visible region]

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. An electron in hydrogen atom first jumps from second excited state to first excited state and then, from first excited state to ground state. Let the ratio of wavelength, momentum and energy of photons in the two cases by x, y and z, then select the wrong answers:

(*a*) z = 1/x (*b*) x = 9/4

(*c*) y = 5/27 (*d*) z = 5/27

2. A particle of $\frac{e}{m}$ ratio equal to 4×10^5 coul/kg is accelerated from rest through a potential difference of 20 volt. The speed of particle is:

(*a*) 4.0 m/s (*b*) 4000 km/s

(*c*) 4000 cm/s (*d*) 4000 m/s

3. For a 3s-orbital, value of ψ is given by following relation :

$$\psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{1}{a_0}\right)^{3/2}(6-6\sigma+\sigma^2)e^{-\sigma/2};\ \text{where } \sigma = \frac{2r\cdot Z}{3a_0}$$

What is the maximum radial distance of node from nucleus?

(*a*) $\frac{(3+\sqrt{3})a_0}{Z}$ (*b*) $\frac{a_0}{Z}$

(*c*) $\frac{3}{2}\frac{(3+\sqrt{3})a_0}{Z}$ (*d*) $\frac{2a_0}{Z}$

4. The radial part $R(r) = \frac{1}{9\sqrt{6}a_0^{3/2}}\left(\frac{6r}{a_0} - \frac{r^2}{a_0^2}\right)e^{-r/3a_0}$ represent which orbital—

(*a*) 3s (*b*) 3d (*c*) 3p (*d*) 2s

5. The angular momentum of electron in Bohr's orbit is J. What will be the K.E. of electron in that Bohr's orbit?

(*a*) $\frac{1}{2}\frac{Jv}{r}$ (*b*) $\frac{Jv}{r}$ (*c*) $\frac{J^2}{2m}$ (*d*) $\frac{J^2}{2r}$

6. Select the correct statement(s):

(*a*) All electromagnetic radiation travel with speed of light in vacuum.

(*b*) Energy of photon of UV light is lower than that of yellow light.

(*c*) He^+ and H have similar spectrum.

(*d*) The total energy of an electron in unielectronic specie is greater than zero.

7. Which is **correct** statement:

(*a*) The difference in angular momentum associated with the electron present in consecutive orbits of H-atom is $(n-1)\frac{h}{2\pi}$.

(*b*) Energy difference between energy levels will be changed if, P. E. at infinity assigned value other than zero.

(*c*) Frequency of spectral line in a H-atom is in the order of $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$.

(*d*) On moving away from the nucleus, kinetic energy of electron increases.

8. The ratio of the radius of Bohr first orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of H nucleus) is approximately:

(*a*) 1 : 1 (*b*) 1 : 2 (*c*) 2 : 1 (*d*) 1 : 4

9. A unielectronic species is in some excited state 'A' and on absorbing a photon of energy 'x' eV gets promoted to a new state 'B'. On de-excitation back to the ground state, a total of 10 different wavelengths were emitted in which seven have energy greater than 'x' eV. What will be the ionisation energy of the species?

(*a*) 25 x eV (*b*) $\frac{225}{16}$x eV

(*c*) $\frac{25}{16}$x eV (*d*) 25 × 9 x eV

10. The Schrodinger wave equation for hydrogen atom of 4s-orbital is given by:

$$\Psi(r) = \frac{1}{16\sqrt{4}}\left(\frac{1}{a_0}\right)^{3/2} \quad [(\sigma - 1)(\sigma^2 - 8\sigma + 12)]e^{-\sigma/2}$$

where a_0 = 1st Bohr radius and $\sigma = \frac{2r}{a_0}$. The distance from the nucleus where there will be no radial node will be:

(*a*) $r = \frac{a_0}{2}$ (*b*) $r = 3a_0$ (*c*) $r = a_0$ (*d*) $r = 2a_0$

11. An orbital is found to contain total nodes = 3 and radial nodes = 1. Orbital angular momentum for the electron present in this orbital is:

(*a*) 0 (*b*) $\frac{h}{2\pi}\sqrt{6}$ (*c*) $\frac{h}{2\pi}\sqrt{2}$ (*d*) $\frac{h}{4\pi}\sqrt{6}$

12. Select the correct order of initials T(True) or F(False) for following statements—

(I) R(r) v/s 'r' curve for 3s intersect x-axis at 2 points other than infinity

(II) The distance of maximum probability for 3s is higher than 3p.

(III) Radial probability density of electron belonging to 2s is zero at nucleus.

(IV) Outside any orbital probability of finding an electron is exactly zero.

(*a*) FTFT (*b*) TTTF

(c) TTFF (*d*) TFTF

13. Select the incorrect curve:

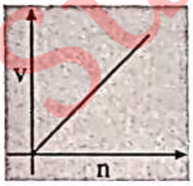
If v = velocity of electron in Bohr's orbit.

r = Radius of electron in Bohr's orbit.

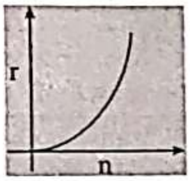
P.E. = Potential energy of electron in Bohr's orbit.

K.E. = Kinetic energy of electron in Bohr's orbit.

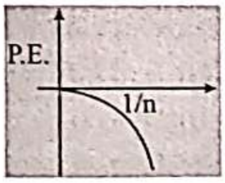
(*a*)



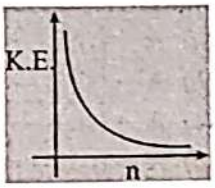
(*b*)



(*c*)



(*d*)



MULTIPLE CORRECT TYPE QUESTIONS

14. Which are correct statements?

(*a*) Hund's rule deals with degenerate orbitals.

(*b*) Pauli exclusion principal stated that only two electrons may exist in the same orbital and these electrons must have opposite spin.

(*c*) In ground state of an atom, the orbitals are filled on the basis of increasing (n + l) value.

(*d*) The maximum number of electrons in the subshell with principal quantum number 'n' is equal to $2n^2$.

15. Which statements are correct?

(*a*) ψ (orbital wave function) is a mathematical function of co–ordinates of the electron.

(*b*) ψ^2 represents probability density of electron at a point.

(*c*) Schrodinger wave equation play same role in quantum mechanics as Newton's Law of motion do in classical mechanics.

(*d*) None of these

16. Choose the correct statements from among the following:

(*a*) The total number of spherical nodes in an orbital are n – *l* – 1.

(*b*) The total number of angular nodes in an orbital are *l*.

(*c*) The number of maxima in an orbital is (n – *l*).

(*d*) A node is a point in space where the wave function ψ has zero amplitude.

17. When photons of energy 4.25 eV strikes the surface of a metal 'A', the ejected photoelectrons have maximum kinetic energy T_A (in eV) and de-Broglie wavelength λ_A. The maximum kinetic energy of photoelectrons liberated from another metal 'B' by photons of energy 4.20 eV is T_B (= T_A – 1.50 eV). If the de-Broglie wave length of these photoelectrons is λ_B (= $2\lambda_A$), then

(*a*) The work function of 'A' is 2.25 eV

(*b*) The work function of 'B' is 3.70 eV

(*c*) T_A = 2.00 eV

(*d*) T_B = 2.75 eV

18. Which is/are correct for sodium atom in the ground state?

(*a*) There is only one unpaired electron.

(*b*) There are five pairs of electrons.

(*c*) 6 electrons are of one spin and other 5 are of opposite spin.

(*d*) There are ten electrons of the same spin.

19. If there are only two H-atoms, each is in 3rd excited state then:

(*a*) Maximum number of different photons emitted is 4.

(*b*) Maximum number of different photos emitted is 3.

(*c*) Minimum number of different photons emitted is 1.

(*d*) Minimum number of different photons emitted is 2.

20. In the experiment on photoelectric effect using light having frequency greater than the threshold frequency, the photocurrent will certainly increase when:

(*a*) Anode voltage is increased.

(*b*) Area of cathode surface is increased.

(*c*) Intensity of incident light is increased.

(*d*) Distance between anode and cathode is increased.

H.W **21.** Which of the following statements is/are correct for an electron of quantum numbers n = 4 and m = 2?

[✓ (a)] The value of ℓ may be 2.

[✓ (b)] The value of ℓ may be 3.

[✓ (c)] The value of s may be +1/2.

(d) The value of ℓ may be 0, 1, 2, 3.

22. Which of the following statement(s) is (are) correct?

(a) The electronic configuration of Cr is $[Ar] (3d)^5 (4s)^1$. (Atomic number of Cr = 24)

(b) The magnetic quantum number may have negative values.

(c) In silver atom, 23 electrons have spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)

(d) None of these

23. The radius of which of the following orbits are double as that of the first Bohr's orbit of hydrogen atom?

(a) He^+ (n = 2) (b) Be^{+3} (n = 2)

(c) O^{+7} (n = 4) (d) C^{+5} (n = 3)

24. Which of the following statements are correct about the cathode ray experiment?

(a) The cathode rays starts from anode and move towards cathode.

(b) Television picture tubes are cathode ray tubes and pictures result due to fluorescence on the television screen coated with certain fluorescent materials.

(c) In the presence of magnetic or electric field, the behaviour of cathode rays are similar to negatively charged particles.

(d) The characteristics of cathode rays does not depend upon the material of electrodes but depend upon nature of gas present in the cathode ray tube.

25. The energy of an electron in the first Bohr's orbit of H-atom is –13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr's orbits of hydrogen is:

(a) –3.4 eV (b) –10.2 eV

(c) –1.51 eV (d) –0.85 eV

26. Which of the following statement(s) is/are correct?

(a) The ratio of the radii of the first three Bohr orbits of hydrogen atom is 1:8:27.

(b) The ratio of magnitude of total energy: kinetic energy: potential energy for electron in any orbit of hydrogen atom is 1:1:2.

(c) If the frequency of a green light is 6×10^{14} Hz, then its wavelength is 500 nm.

(d) The ratio of de Broglie wavelength of a H-atom, He-atom and CH_4-molecule moving with equal kinetic energy is 4 : 2 : 1.

27. The qualitative order of de-Broglie wavelength for electron, proton and α particle is $\lambda_e > \lambda_p > \lambda_\alpha$ if:

(a) If kinetic energy is same for all particles.

(b) If the accelerating potential difference 'V' is same for all the particles (starting from rest).

(c) If velocities are same for all particles.

(d) None of the above.

28. Choose the correct statement among the following:

(a) Radii of max probability: $(r_{max})_{3s} < (r_{max})_{3p} < (r_{max})_{3d}$

(b) $\psi^2(r)$ give probability density at a particular distance over a spherical surface.

(c) For 's' orbitals, $\psi(r)\psi(\theta)\psi(\phi) = \psi(x, y, z)$ is independent of θ and ϕ.

(d) '2p' orbital with quantum numbers. n = 2, l = 1, m = 0, shows angular dependence.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 29 to 32): The wave function for an atomic orbital of single electron atom or ion is

$$\Psi(r,\theta,\phi) = \frac{2}{3}\left(\frac{Z}{3a_0}\right)^{3/2} (1-\sigma)(12-8\sigma+\sigma^2).\sigma.e^{-\sigma/2}.\cos\theta$$

where $\sigma = \left(\frac{2Zr}{na_0}\right)$ and $a_0 = 0.529$ Å. All other parameters have their usual meaning.

29. The number of radial and angular nodes for the orbital is, respectively,

(a) 3, 1 (b) 2, 1 (c) 3, 2 (d) 2, 2

30. The atomic orbital should be:

(a) 4p (b) 5p (c) 5d (d) 5f

31. If θ is the angle measured from Z-axis, then the orbital should be:

(a) p_x (b) p_y (c) p_z (d) d_{z^2}

32. The maximum distance of radial node from the nucleus is:

(a) $\frac{a_0}{Z}$ (b) $\frac{3a_0}{Z}$ (c) $\frac{6a_0}{Z}$ (d) $\frac{15a_0}{Z}$

MATCH THE COLUMN TYPE QUESTIONS

H.W **33.** Match Column-I with Column-II and select the correct answer using the codes given below in the lists (n, ℓ and m are respectively the principal, azimuthal and magnetic quantum no.)

	Column-I		Column-II
A.	Number of values of ℓ for an energy level (n)	p.	0, 1, 2, ... (n – 1)
B.	Values of ℓ for a particular type of orbit	q.	$+\ell$ to $-\ell$ through zero
C.	Number of value of m for ℓ = 2	r.	5
D.	Values of 'm' for a particular type of orbital	s.	n

(a) A → (r); B → (p); C → (s); D → (q)

(b) A → (s); B → (q); C → (r); D → (p)

[✓ (c)] A → (s); B → (p); C → (r); D → (q)

(d) A → (r); B → (p); C → (s); D → (q)

34. Match the column & choose the correct option among the options given.

	Column-I		Column-II
A.	5 → 1 transition in H atom	p.	spectral line in IR region
B.	7 → 3 transition in H atom	q.	spectral line in visible region
C.	Last line of Balmer series in H atom	r.	spectral line in ultra violet region
D.	4 → 2 transition in He$^+$ ion		

(*a*) A → (r); B → (q); C → (r); D → (p)
(*b*) A → (r); B → (p); C → (q); D → (r)
(*c*) A → (r); B → (r); C → (p); D → (r)
(*d*) A → (r); B → (r); C → (p); D → (q)

35. Frequency = 'f' and Time period = 'T', Energy of nth orbit = 'E_n', radius of nth orbit = 'r_n', Atomic number = 'Z', Orbit number = 'n'.

	Column-I		Column-II (proportional to)
A.	f	p.	n^3
B.	T	q.	Z^2
C.	$\lvert E_n \rvert$	r.	$\frac{1}{n^2}$
D.	$\frac{1}{r_n}$	s.	Z

(*a*) A → (q); B → (p); C → (q,r); D → (r,s)
(*b*) A → (r); B → (p); C → (q,r); D → (r,s)
(*c*) A → (q); B → (p); C → (q,r); D → (q, s)
(*d*) A → (q); B → (p); C → (s,r); D → (r,s)

36. Match the column & choose the correct option among the options given.

	Column-I (For mono electronic species)		Column-II
A.	Radius of nth orbit	p.	inversely proportional to Z
B.	Magnitude of energy of electron in nth orbit	q.	inversely proportional to n^2
C.	Velocity of electron in nth orbit	r.	inversely proportional to n
D.	Angular momentum of electron in nth orbit	s.	proportional to n

(*a*) A → (p); B → (q); C → (r); D → (s)
(*b*) A→ (p,r); B → (q); C → (r); D → (s)
(*c*) A → (p,q); B → (p,r); C → (r); D → (s)
(*d*) A → (p,q); B → (q); C → (s); D → (r)

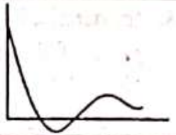
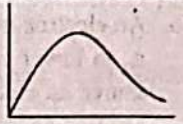
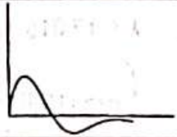
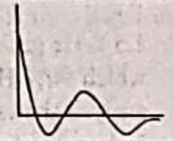
41.W

37. Match the column & choose the correct option among the options given.

	Column-I		Column-II
A.	Orbit angular momentum	p.	$\sqrt{n(n+2)}$ B.M.
B.	Orbital angular momentum	q.	$\frac{nh}{2\pi}$
C.	Spin angular momentum	r.	$\sqrt{s(s+1)}\hbar$
D.	Magnetic moment	s.	$\sqrt{l(l+1)}\hbar$
		t.	$\sqrt{n(n+1)}\hbar$

(*a*) A → (p); B → (r); C → (s); D → (q)
(*b*) A → (p); B → (s); C → (r); D → (q)
(*c*) A → (q); B → (s); C → (r); D → (p)
(*d*) A → (q); B → (r); C → (s); D → (p)

38. Match the columns & choose the correct option among the options given.

	Column-I (Orbital)		Column-II (R vs. r Graph)
A.	3s	p.	
B.	4s	q.	
C.	2p	r.	
D.	3p	s.	

(*a*) A → (q); B → (s); C → (p); D → (r)
(*b*) A → (p); B → (q); C → (s); D → (r)
(*c*) A → (r); B → (s); C → (q); D → (p)
(*d*) A → (p); B → (s); C → (q); D → (r)

INTEGER TYPE QUESTIONS

39. What is likely to be orbit number for a circular orbit of diameter 20 nm of the hydrogen atom if we assume Bohr orbit to be the same as that represented by the principal quantum number?

40. Find the quantum number (n) corresponding to the excited state of He$^+$ ion if on transition to the ground state, that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm

41. Find the atomic number of hydrogen-like ion which has the wavelength difference between the first line of Balmer and Lyman series equal to 59.3 nm.

42. The diameter of a dust particle of mass 10^{-3} gm is 2Å. If uncertainity in speed of this particle is $\frac{3.31}{\pi} \times 10^{-3}$ m/s, then find minimum uncertainity in its position (in terms of 10^{-26} m).

43. A hydrogen-like atom with (atomic number Z) is present in the higher excited state of quantum number n. This excited state atom can make a transition to the 1st excited state by successively emitting two photons of energies 10 eV and 17eV, respectively. Alternatively, the atom from the same excited state can make a transition to 2nd excited state by emitting two photons of energies 4.25 eV and 5.95 eV, respectively. Find sum of Z and n.

44. If a metal is exposed with light of wavelength λ, the maximum kinetic energy produced is found to be 2 eV. When the same metal is exposed to a wavelength $\frac{\lambda}{5}$ the maximum kinetic energy was found to be 14 eV. Find the value of work function (in eV).

45. 'α particle' of 3.6 MeV are fired towards nucleus ${}_{Z}^{A}X$ at point of closest separation distance between 'α particle' and 'X' is 1.6×10^{-14}m. Calculate atomic number of 'X' [Given: $1/4\pi\varepsilon_0 = 9 \times 10^9$ in S.I. units]

46. An electron in Li^{2+} ion makes a transition from higher state n_2 to lower state $n_1 = 6$. The emitted photons is used to ionize an electron in H–atom from 2nd excited state. The electron on leaving the H–atom has a de–Broglie wavelength λ = 12.016 Å. Find the value of n_2.

$$\left(\text{use } (12.016^2) = \frac{150 \times 144}{13.6 \times 11}, \lambda_e = \frac{150}{\sqrt{KE_{ev}}}\right)$$

47. 1.5 L He gas is taken at 500K and 560 mm Hg pressure in which 90% He are converted into He^+ ions. Spectral line analysis shows that 85% ions exist in the 3rd level, 10% in the 2nd level and rest in the ground level. Calculate the total energy (in kJ) evolved when all ions return back to ground state.

48. Infrared lamps are used in restaurants to keep the food warm. The infrared radiation is strongly absorbed by water, raising its temperature and that of the food. If the wavelength of infrared radiation is assumed to be 1500 nm, then the number of photons per second of infrared radiation produced by an infrared lamp that consumes energy at the rate of 100 W and is 12% efficient only is x × 10^{19}. Find the value of x.

49. The dye acriflavine, when dissolved in water, has its maximum light absorption at 4530 Å and its maximum fluorescence emission at 5080 Å. The number of fluorescence quanta is, on the average, 53% of the number of quanta absorbed. Using the wavelengths of maximum absorption and emission, what percentage of absorbed energy is emitted as fluorescence?

50. The average life time for n = 3 excited state of a hydrogen-like atom is 4.8×10^{-8} s and that for the n = 2 state is 1.28×10^{-7} s. Ratio of the average number of revolutions made in the n = 3 state to the average number of revolutions made in the n = 2 state before any transitions can take place from these states is 1 : x. The value of x is

51. Suppose a satellite is in geostationary orbit at an average distance of 12600 km from the earth surface. This satellite is telecasting a cricket match between India and Pakistan. The radiowaves from the stadium are first received by the satellite and then from satellite to our TV sets. If a batsman hits a ball, then after what time (approximate, in milliseconds), we will see this action in our TV sets?

52. In a sample of H-atoms in ground state, electrons make transition from ground state to a particular excited state where path length is 5 times de Broglie wavelength, electrons make back transition to the ground state producing all possible photons. If photon having 2nd highest energy of this sample can be used to excite the electron in a particular excited state of Li^{2+} ion then find the final excited state of Li^{2+} ion.

53. In a container a mixture is prepared by mixing of three samples of hydrogen, helium ion (He^+) and lithium ion (Li^{2+}). In sample, all the hydrogen atoms are in 1st excited state all the He^+ ions are in third excited state and all the Li^{2+} ions are in fifth excited state. Find the total number of different spectral lines observed in the emission spectrum of such a sample, when the electrons return back to the ground state.

54. In a hypothetical H-atom, the mass of electron & its charge is double of what we consider then calculate the magnitude of total energy (in eV) of electron in the Ist orbit of such a hypothetical H-atom?

[Assuming all others concepts and parameter to be same as we considered in Bohr's model.]

55. The critical wavelength for producing photoelectric effect in a metal is 2500Å. What wavelength (in Å)would be necessary to produce photoelectric effect from this metal, having twice the K.E. of those produced at 2000 Å.

PYQ's (Past Year Questions)

SUB-ATOMIC PARTICLES AND ATOMIC MODELS

1. Given below are two statements: one is labelled as assertion and the other is labelled as reason.

Assertion (A): Loss of electron from hydrogen atom results in nucleus of ~1.5×10^{-3} pm size.

Reason (R): Proton (H^+) always exists in combined form

In the light of the above statements, choose the most appropriate answer from the options given below:

[6 April, 2023 (Shift-I)]

(*a*) Both (A) and (R) are correct and (R) is the correct explanation of (A)

(*b*) (A) is correct but (R) is not correct

(*c*) (A) is not correct but (R) is correct

(*d*) Both (A) and (R) are correct but (R) is NOT the correct explanation of (A).

2. Electrons in a cathode ray tube have been emitted with a velocity of 1000 ms^{-1}. The number of following statements which is/are true about the emitted radiation is ________ .

Given : $h = 6 \times 10^{-34}$ Js, $m_e = 9 \times 10^{-31}$ kg.

[1 Feb, 2023 (Shift-I)]

(*a*) The de-Broglie wavelength of the electron emitted is 666.67nm

(*b*) The characteristic of electrons emitted depend upon the material of the electrodes of the cathode ray tube

(*c*) The cathode rays start from cathode and move towards anode

(*d*) The nature of the emitted electrons depends on the nature of the gas present in cathode ray tube

3. Consider an imaginary ion $^{14}_{22}X^{3-}$. The nucleus contains 'a'% more neutrons than the number of electrons in the ion. The value of 'a' is________. [nearest integer]

[26 July, 2022 (Shift-II)]

4. If the Thomson model of the atom was correct, then the result of Rutherford's gold foil experiment would have been:

[27 July, 2021 (Shift-II)]

(*a*) All α – particles get bounced back by 180°

(*b*) α – particles are deflected over a wide range of angles

(*c*) All of α – particles pass through the gold foil without decrease in speed

(*d*) α – particles pass through the gold foil deflected by small angles and with reduced speed

5. Amongst the following statements, which was not proposed by Dalton was **[7 Jan, 2020 (Shift-I)]**

(*a*) Matter consists of invisible atoms

(*b*) When gases combine or reproduced in a chemical reaction they do so in a simple ratio by volume provided all gases are at the same temperature & pressure

(*c*) Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction

(*d*) All the atoms of a given element have identical properties including identical mass Atoms of different elements differ in mass

DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

6. The ionization energy of sodium in kJ mol^{-1}. If electromagnetic radiation of wavelength 242 nm is just sufficient to ionize sodium atom is______. **[31 Jan, 2024 (Shift-I)]**

7. Match **List-I** with **List-II**.

	List-I Alkali Metal		List-II Emission Wavelength (in nm)
A.	Li	I	589.2
B.	Na	II.	455.5
C.	Rb	III.	670.8
D.	Cs	IV.	780.0

Choose the **correct** answer from the options given below:

[06 April, 2024 (Shift-II)]

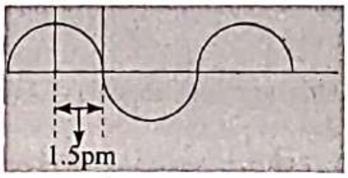
(*a*) (A)-(I), (B)-(IV), (C)-(III), (D)-(II)

(*b*) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)

(*c*) (A)-(IV), (B)-(II), (C)-(I), (D)-(III)

(*d*) (A)-(II), (B)-(IV), (C)-(III), (D)-(I)

8. A hypothetical electromagnetic wave is shown below.



The frequency of the wave is x × 10^{19} Hz.

x = ________ (nearest integer). **[08 April, 2024 (Shift-I)]**

9. Wavenumber for a radiation having 5800 Å wavelength is $x \times 10$ cm^{-1}. The value of x is ________.

[08 April, 2024 (Shift-II)]

10. Given below are two statements: one is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**:

Assertion (A): In the photoelectric effect, the electrons are ejected from the metal surface as soon as the beam of light of frequency greater than threshold frequency strikes the surface.

Reason (R): When the photon of any energy strikes an electron in the atom, transfer of energy from the photon to the electron takes place. **[11 April, 2023 (Shift-I)]**

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) Both (A) and (R) are correct but (R) is NOT the correct explanation of (A)

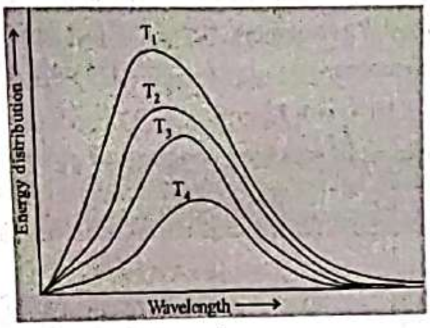
(*b*) (A) is correct but (R) is not correct

(*c*) Both (A) and (R) are correct and (R) is the correct explanation of (A)

(*d*) (A) is not correct but (R) is correct

11. Following figure shows spectrum of an ideal black body at four different temperatures. The number of correct statement/s from the following is _______.

[24 Jan, 2023 (Shift-II)]



(*a*) $T_4 > T_3 > T_2 > T_1$

(*b*) The black body consists of particles performing simple harmonic motion

(*c*) The peak of the spectrum shifts to shorter wavelength as temperature increases

(*d*) $\frac{T_1}{V_1} = \frac{T_2}{V_2} = \frac{T_3}{V_3} \neq$ constant

(*e*) The given spectrum could be explained using quantisation of energy

12. The minimum energy that must be possessed by photons in order to produce the photoelectric effect with platinum metal is:

[Given: The threshold frequency of platinum is $1.3 \times 10^{15}\ s^{-1}$ and $h = 6.6 \times 10^{-34}$ J s.]

[25 June, 2022 (Shift-II)]

(*a*) 3.21×10^{-14} J

(*b*) 6.24×10^{-16} J

(*c*) 8.58×10^{-19} J

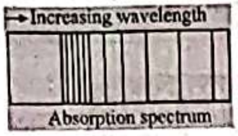
(*d*) 9.76×10^{-20} J

13. A proton and a Li^{3+} nucleus are accelerated by the same potential. If λ_{Li} and λ_P denote the de-Broglie wavelengths of Li^{3+} and proton respectively, then the value of $\frac{\lambda_{Li}}{\lambda_P}$ is $x \times 10^{-1}$. The value of x is _________(Rounded off to the nearest integer) [Mass of Li^{3+} = 8.3 times mass of proton]

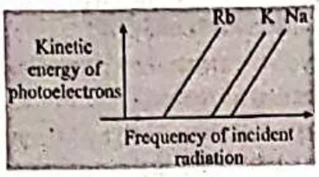
[24 Feb, 2021 (Shift-I)]

14. The figure that is not a direct manifestation of the quantum nature of atoms is: **[2 Sept, 2020 (Shift-I)]**

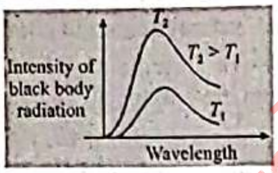
(*a*)



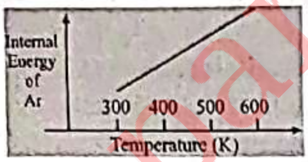
(*b*)



(*c*)



(*d*)



15. The de-Broglie wavelength (λ) associated with a photoelectron varies with the frequency (v) of the incident radiation as [v_0 is threshold frequency]:

[11 Jan, 2019 (Shift-II)]

(*a*) $\lambda \propto \frac{1}{(v - v_0)}$

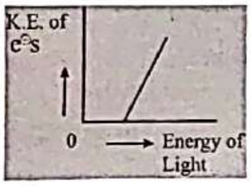
(*b*) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{4}}}$

(*c*) $\lambda \propto \frac{1}{(v - v_0)^{\frac{3}{2}}}$

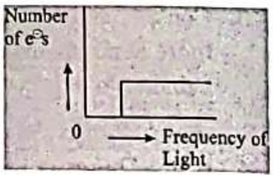
(*d*) $\lambda \propto \frac{1}{(v - v_0)^{\frac{1}{2}}}$

16. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? **[10 Jan, 2019 (Shift-I)]**

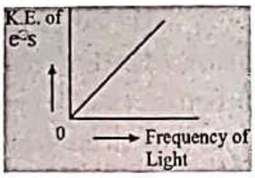
(*a*)



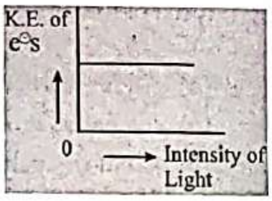
(*b*)



(*c*)



(*d*)



17. Consider a Helium (He) atom that absorbs a photon of wavelength 330 nm. The change in the velocity (in cm s^{-1}) of He atom after the photon absorption is _____.

(Assume: Momentum is conserved when photon is absorbed).

Use: Planck constant = 6.6×10^{-34} Js, Avogadro number = $6 \times 10^{23}\ mol^{-1}$, molar mass of He = 4 g mol^{-1}

[JEE Adv 2021]

BOHR'S MODEL FOR HYDROGEN ATOM

18. Match List-I with List-II

List-I (Spectral Series for Hydrogen)		List-II (Spectral Region/ Higher Energy State)	
A.	Lyman	I.	Infrared region
B.	Balmer	II.	UV region
C.	Paschen	III.	Infrared region
D.	Pfund	IV.	Visible region

Choose the correct answer from the options given below: **[29 Jan, 2024 (Shift-II)]**

(*a*) A-II, B-III, C-I, D-IV (*b*) A-I, B-III, C-II, D-IV

(*c*) A-II, B-IV, C-III, D-I (*d*) A-I, B-II, C-III, D-IV

19. Number of spectral lines obtained in He^+ spectra. When an electron makes transition from fifth excited state to first excited state will be ________. **[30 Jan, 2024 (Shift-II)]**

20. Frequency of the de-Broglie wave of electron in Bohr's first orbit of hydrogen atom is _______ $\times 10^{13}$ Hz (nearest integer).

[Given: R_H (Rydberg constant) = 2.18×10^{-18} J. *h* (Planck's constant) = 6.6×10^{-34} J.s.] **[06 April, 2024 (Shift-I)]**

21. The de-Broglie's wavelength of an electron in the 4th orbit is ________ πa_0. (a_0 = Bohr's radius) **[04 April, 2024 (Shift-I)]**

22. The value of Rydberg constant (R_H) is 2.18×10^{-18} J. The velocity of electron having mass 9.1×10^{-31} kg in Bohr's first orbit of hydrogen atom = ______ $\times 10^5$ ms^{-1} (nearest integer) **[05 April, 2024 (Shift-I)]**

23. For hydrogen atom, energy of an electron in first excited state is –3.4eV, K.E. of the same electron of hydrogen atom is xeV. Value of x is _________ $\times 10^{-1}$ eV (Nearest integer). **[06 April, 2024 (Shift-II)]**

24. Given below are two statements:

Statement-I: According to Bohr's model of hydrogen atom, the angular momentum of an electron in a given stationary state is quantised.

Statement-II: The concept of electron in Bohr's orbit, violates the Heisenberg uncertainty principle. In the light of the above statements, choose the most appropriate answer from the options given below: **[15 April, 2023 (Shift-I)]**

(*a*) Both Statement-I and Statement-II are correct

(*b*) Statement-I is correct but Statement-II is incorrect

(*c*) Statement-I is incorrect but Statement-II is correct

(*d*) Both Statement-I and Statement-II are incorrect

25. If the radius of the 3rd Bohr's orbit of hydrogen atom is r_3 and the radius of 4th Bohr's orbit is r_4. Then: **[26 June, 2022 (Shift-I)]**

(*a*) $r_4 = \frac{9}{16} r_3$ (*b*) $r_4 = \frac{16}{9} r_3$

(*c*) $r_4 = \frac{3}{4} r_3$ (*d*) $r_4 = \frac{4}{3} r_3$

26. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is equal to $\frac{h^2}{xma_0^2}$. The value of 10x is ________. (a_0 is radius of Bohr's orbit) (Nearest integer) [Given : $\pi = 3.14$] **[27 Aug, 2021 (Shift-I)]**

27. For the Balmer series in the spectrum of H-atom, $\bar{v} = R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$ the correct statements among (I) to (IV) are: **[8 Jan, 2020 (Shift-I)]**

(I) As wavelength decreases, the lines in the series converge

(II) The integer n_1 is equal to n_2

(III) The lines of longest wavelength corresponds to $n_2 = 3$

(IV) The ionization energy of hydrogen can be calculated from wave number of these lines

(*a*) (II), (III), (IV) (*b*) (I), (III), (IV)

(*c*) (I), (II), (III) (*d*) (I), (II), (IV)

28. The de-Broglie wavelength of an electron in the 4th Bohr orbit is: **[9 Jan, 2020 (Shift-I)]**

(*a*) $6\pi a_0$ (*b*) $4\pi a_0$

(*c*) $2\pi a_0$ (*d*) $8\pi a_0$

29. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose?

[$R_H = 1 \times 10^5$ cm^{-1}, $h = 6.6 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms^{-1}] **[11 Jan, 2019 (Shift-I)]**

(*a*) Paschen, $\infty \rightarrow 3$ (*b*) Paschen, $5 \rightarrow 3$

(*c*) Balmer, $\infty \rightarrow 2$ (*d*) Lyman, $\infty \rightarrow 1$

30. For He^+, a transition takes place from the orbit of radius 105.8 pm to the orbit of radius 26.45 pm. The wavelength (in nm) of the emitted photon during the transition is ___.

[Use: Bohr radius, a = 52.9 pm

Rydberg constant, $R_H = 2.2 \times 10^{-18}$ J

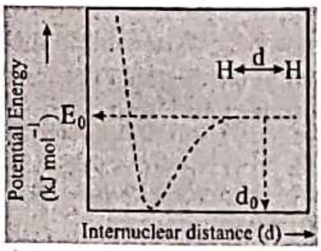
Planck's constant, $h = 6.6 \times 10^{-34}$ J s

Speed of light, $c = 3 \times 10^8$ m s^{-1}] **[JEE Adv 2023]**

31. The figure below is the plot of potential energy versus internuclear distance (d) of H_2 molecule in the electronic ground state. What is the value of the net potential energy E_0 (as indicated in the figure) in kJ mol^{-1}, for $d = d_0$ at which the electron-electron repulsion and the nucleus-nucleus repulsion energies are absent? As reference, the potential energy of H atom is taken as zero when its electron and the nucleus are infinitely far apart.

Use Avogadro constant as 6.023×10^{-23} mol^{-1}.

[JEE Adv 2020]



Comprehension (Q. 32 to 33): Answer the following by appropriately matching the lists based on the information given in the paragraph

Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following Column-I contains some quantities for the n^{th} orbit of the atom and Column-II contains options showing how they depend on n. **[JEE Adv 2019]**

Column-I		Column-II	
(I)	Radius of the n^{th} orbit.	(P)	$\propto n^{-2}$
(II)	Angular momentum of the electron in the n^{th} orbit.	(Q)	$\propto n^{-1}$
(III)	Kinetic energy of the electron in the n^{th} orbit.	(R)	$\propto n^{0}$
(IV)	Potential energy of the electron in the n^{th} orbit.	(S)	$\propto n^{1}$
		(T)	$\propto n^{2}$
		(U)	$\propto n^{1/2}$

32. Which of the following options has the correct combination considering List-I and List-II?

(*a*) (II), (R) (*b*) (I), (P) (*c*) (I), (T) (*d*) (II), (Q)

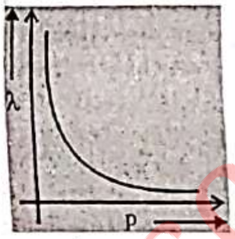
33. Which of the following options has the correct combination considering List-I and List-II?

(*a*) (III), (S) (*b*) (IV), (Q) (*c*) (IV), (U) (*d*) (III), (P)

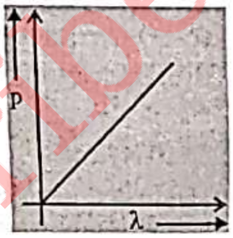
OWARDS QUANTUM MECHANICAL ODEL OF THE ATOM

34. According to the wave-particle duality of matter by de-Broglie, which of the following graph plot presents most appropriate relationship between wavelength of electron (λ) and momentum of electron (p)? **[01 Feb, 2024 (Shift-I)]**

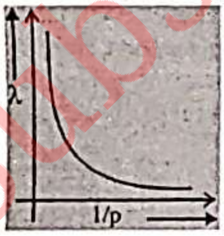
(*a*)



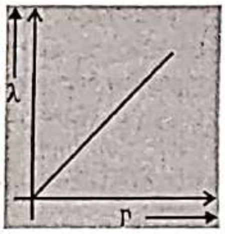
(*b*)



(*c*)



(*d*)



35. Based on Heisenberg's uncertainty principle, the uncertainty in the velocity of the electron to be found within an atomic nucleus of diameter 10^{-15} m is ______ $\times 10^{9}$ ms^{-1} (nearest integer)

[Given: mass of electron = 9.1×10^{-31} kg, Planck's constant (h) = 6.626×10^{-34} Js]

36. The wave function (Ψ) of 2s is given by

$$\psi_{2s} = \frac{1}{2\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{1/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

At $r = r_0$, radial node is formed. Thus, r_0 in terms of a_0 **[30 Jan, 2023 (Shift-II)]**

(*a*) $r_0 = a_0$ (*b*) $r_0 = 4a_0$

(*c*) $r_0 = \frac{a_0}{2}$ (*d*) $r_0 = 2a_0$

37. The minimum uncertainty in the speed of an electron in an one dimensional region of length $2a_0$ (Where a_0 = Bohr radius 52.9 pm) is __________ km s^{-1}.
(Given: Mass of electron = 9.1×10^{-31} kg, Planck's constant, h = 6.63×10^{-34}Js) **[29 July, 2022 (Shift-I)]**

38. An accelerated electron has speed of 5×10^{6} ms^{-1} with an uncertainty of 0.02%. The uncertainty in finding its location while in motion is $x \times 10^{-9}$ m. The value of x is ________. (Nearest integer)
[Use mass of electron = 9.1×10^{-31} kg, h = 6.63×10^{-34} Js, π = 3.14] **[25 July, 2021 (Shift-II)]**

QUANTUM MECHANICAL MODEL OF THE ATOM

H.W **39.** The number of electrons present in all the completely filled subshells having $n = 4$ and $s = +\frac{1}{2}$ is 16.
(Where n = principal quantum number and s = spin quantum number) **[27 Jan, 2024 (Shift-I)]**

H.W **40.** The correct set of four quantum numbers for the valence electron of rubidium atom (Z = 37) is: **[29 Jan, 2024 (Shift-I)]**

[✓ (*a*)] $5, 0, 0, +\frac{1}{2}$

(*b*) $5, 0, 1, +\frac{1}{2}$

(*c*) $5, 1, 0, +\frac{1}{2}$

(*d*) $5, 1, 1, +\frac{1}{2}$

41. Given below are two statements:

Statement-I: The orbitals having same energy are called as degenerate orbitals.

Statement-II: In hydrogen atom, 3p and 3d orbitals are not degenerate orbitals.

In the light of the above statements, choose the **most appropriate** answer from the options given **[30 Jan, 2024 (Shift-I)]**

(*a*) Statement-I is true but Statement-II is false
(*b*) Both Statement-I and Statement-II are true.
(*c*) Both Statement-I and Statement-II are false
(*d*) Statement-I is false but Statement-II is true

H.W **42.** The four quantum numbers for the electron in the outer most orbital of potassium (atomic no. 19) are

[31 Jan, 2024 (Shift-II)]

(*a*) $n = 4, l = 2, m = -1, s = +\frac{1}{2}$

[✓ (*b*)] $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(*c*) $n = 3, l = 0, m = 1, s = +\frac{1}{2}$

(*d*) $n = 2, l = 0, m = 0, s = +\frac{1}{2}$

43. The number of radial node/s for 3p orbital is:

[01 Feb, 2024 (Shift-II)]

(*a*) 1 (*b*) 4 (*c*) 2 (*d*) 3

H.W **44.** The maximum number of orbitals which can be identified with $n = 4$ and $m_l = 0$ is 4 **[04 April, 2024 (Shift-II)]**

H.W **45.** In an atom, total number of electrons having quantum numbers $n = 4, |m_l| = 1$ and $m_s = -1/2$ is 6

[05 April, 2024 (Shift-II)]

H.W **46.** Compare the energies of following sets of quantum numbers for multielectron system. **[09 April, 2024 (Shift-I)]**

(A) $n = 4, l = 1$ (B) $n = 4, l = 2$

(C) $n = 3, l = 1$ (D) $n = 3, l = 2$

(E) $n = 4, l = 0$

Choose the correct answer from the options given below:

(*a*) (B) > (A) > (C) > (E) > (D)

(*b*) (E) > (C) < (D) < (A) < (B)

[✓ (*c*)] (E) > (C) > (A) > (D) > (B)

[✓ (*d*)] (C) < (E) < (D) < (A) < (B)

H.W **47.** Arrange the following orbitals in decreasing order of energy?

[31 Jan, 2023 (Shift-II)]

(A) $n = 3, l = 0, m = 0$ (B) $n = 4, l = 0, m = 0$

(C) $n = 3, l = 1, m = 0$ (D) $n = 3, l = 2, m = 1$

The correct option for the order is:

(*a*) B > D > C > A [✓ (*b*)] D > B > C > A

(*c*) A > C > B > D (*d*) D > B > A > C

H.W **48.** Consider the following statements :

[28 June, 2022 (Shift-II)]

(A) The principal quantum number 'n' is a positive integer with values of 'n' = 1, 2, 3, ...

(B) The azimuthal quantum number 'l' for a given 'n' (principal quantum number) can have values as 'l' = 0, 1, 2, ... n

(C) Magnetic orbital quantum number 'm_l' for a particular 'l' (azimuthal quantum number) has $(2l + 1)$values.

(D) ±1/2 are the two possible orientations of electron spin.

(E) For $l = 5$,there will be a total of 9 orbital

Which of the above statements are correct ?

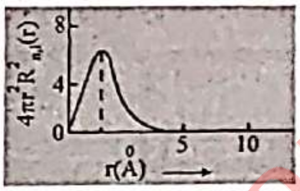
(*a*) (A), (B) and (C) (*b*) (A), (C), (D) and (E)

[✓ (*c*)] (A), (C) and (D) (*d*) (A), (B), (C) and (D)

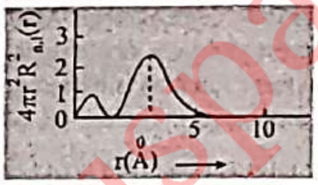
49. The Plots of radial distribution functions for various orbitals of hydrogen atom against 'r' are given below:

[25 Feb, 2021 (Shift-I)]

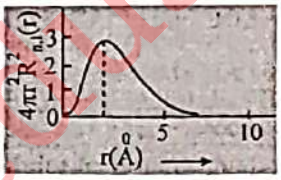
(A)



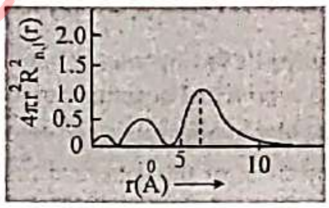
(B)



(C)



(D)



The correct plot for 3s orbital is:

(*a*) (D) (*b*) (B) (*c*) (A) (*d*) (C)

50. The ground state energy of hydrogen atom is –13.6 eV. Consider an electronic state ψ of He^+ whose energy, azimuthal quantum number and magnetic quantum number are –3.4 eV, 2 and 0 respectively. Which of the following statement(s) is(are) true for the state ψ?

[JEE Adv 2019]

(*a*) It has 2 angular nodes

(*b*) It has 3 radial nodes

(*c*) It is a 4d state

(*d*) The nuclear charge experienced by the electron in this state is less than 2e, where e is the magnitude of the electronic charge

PW Challengers

SINGLE CHOICE QUESTIONS

1. Suppose we have a sample containing 10 identical H-like atoms (hypothetical atoms, Z can be fractional), out of which some are in ground state and some others in a higher energy level n. The total energy of electrons in ground state is –48 eV. When the sample is exposed to radiations of wavelength 310 nm, the electrons jump to another higher energy level (n + 3). Upon back-transition, a maximum of 10 different lines are produced. What should be the minimum number of atoms present in energy level n?

   (hc = 12400 eV Å)

   (*a*) 4 (*b*) 3 (*c*) 2 (*d*) 1

INTEGER TYPE QUESTIONS

2. Mr. Alakh Pandey has to decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as;

   $\psi_{(r)} = k_1 \cdot e^{-r/k_2}\left(r^2 - 5k_3r + 6k_3^2\right)$.

   From the following information given about each alphabet write down the answers in the form of "ABCDEF", for above orbital.

   Info A = Value of n where "n" is principal quantum number.

   Info B = No. of angular nodes.

   Info C = Azimuthal quantum number of subshell to which orbital belongs.

   Info D = No. of subshells having energy between (n + 5)s to (n + 5)p where n is principal quantum number.

   Info E = Orbital angular momentum of given orbital.

   Info F = Radial distance of the spherical node which is farthest from the nucleus. (Assuming k_3 = 1unit)

3. The wave function for the electron in the ground state of H-atom is $\psi_{1s} = (\pi a_0^3)^{-1/2} e^{-r/a_0}$. What is the probability (in terms of 10^{-6}) of finding an electron somewhere inside a small sphere of radius 10^{-12} m centred on nucleus?

4. For 3s orbital of hydrogen atom, the normalised wave function is

$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[27 - \frac{18r}{a_0} + \frac{2r^2}{a_0^2}\right]e^{\frac{-r}{3a_0}}$$

   If distance between the radial nodes is d, calculate the value of $\frac{d}{1.73a_0}$.

NUMERICAL TYPE QUESTIONS

5. The normalized wave function for the ground state of hydrogen atom is $\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{\frac{-r}{a_0}}$ where a_0 is the first Bohr radius. Calculate the probability of finding the electron somewhere between 0 and $2a_0$.

   (Answer upto three decimal)

6. The de-Broglie wavelength of electron of He^+ ion is 3.329Å. If the photon emitted upon de-excitation of this He^+ ion is made to hit H-atom in its ground state so as to liberate electron from it, what will be the de-Broglie's wavelength of photoelectron?

   (Answer upto two decimal)

COMPREHENSION BASED QUESTIONS

Comprehension-I

Let us assume a different atomic model in which electron revolves around the nucleus (proton) at a separation r under the action of force which is different from electrostatic force of attraction. The potential energy between an electron and the proton due to this force is given by $U = -k/r^4$, where k is a constant. This hypothetical atom is obeying Bohr's quantization condition.

7. The radius of nth Bohr's orbit is

   (*a*) $r = \frac{\pi}{nh}\sqrt{km}$ (*b*) $r = \frac{2\pi}{nh}\sqrt{km}$

   (*c*) $r = \frac{4\pi}{nh}\sqrt{km}$ (*d*) $r = \frac{8\pi}{nh}\sqrt{km}$

8. The speed of electron in the n^{th} orbit is

   (*a*) $V = \frac{nh}{8\pi^2 m\sqrt{km}}$ (*b*) $V = \frac{n^2h}{8\pi^2 m\sqrt{km}}$

   (*c*) $V = \frac{nh^2}{4\pi^2 m\sqrt{km}}$ (*d*) $V = \frac{n^2h^2}{8\pi^2 m\sqrt{km}}$

9. The total energy of the electron in the n^{th} orbit is

   (*a*) $T.E. = \frac{-n^4h^4}{128\pi^4m^2k}$ (*b*) $T.E. = \frac{n^4h^4}{128\pi^4m^2k}$

   (*c*) $T.E. = \frac{n^4h^4}{256k\pi^4m^2}$ (*d*) $T.E. = \frac{-n^4h^4}{256\pi^4m^2}$

Comprehension-II

The wave function for an atomic orbital of single electron atom or ion is

$$\Psi(r, \theta, \phi) = \frac{2}{3}\left(\frac{Z}{3a_0}\right)^{3/2}(1 - \sigma)(12 - 8\sigma + \sigma^2)\,.\,\sigma\,.\,e^{-\sigma/2}\,.\,\cos\theta$$

where $\sigma = \frac{2Zr}{na_0}$ and $a_0 = 0.529$ Å. All other parameters have their usual meaning

10. The number of radial and angular nodes for the orbital is, respectively.

    (*a*) 3, 1 (*b*) 2, 1 (*c*) 3, 2 (*d*) 2, 2

11. The atomic orbital should be

    (*a*) 4p (*b*) 5p (*c*) 5d (*d*) 5f

12. If θ is the angle measured from Z-axis, then the orbital should be

    (*a*) p_x (*b*) p_y (*c*) p_z (*d*) d_{z^2}

13. The maximum distance of radial node from the nucleus is

(*a*) $\frac{a_0}{Z}$ (*b*) $\frac{3a_0}{Z}$ (*c*) $\frac{6a_0}{Z}$ (*d*) $\frac{15a_0}{Z}$

Comprehension-III

Consider a system containing a negatively charged pion (π^-, $m_\pi = 273\ m_e$) orbiting around a stationary nucleus of atomic number Z. The total energy (E_n) of ion is half of its potential energy (PE_n) in n^{th} stationary state. The motion of the pion can be assumed to be in a uniform circular motion with centripetal force given by the force of attraction between the positive nucleus and the pion. Assume that pion revolves only in the stationary states defined by the quantisation of its angular momentum about the nucleus as per Bohr's model.

14. The magnitude of potential energy (PE_n) of ion follows:

(*a*) $PE_n \propto m_\pi\left(\frac{n^2}{Z}\right)$ (*b*) $PE \propto m_\pi\left(\frac{Z^2}{n^2}\right)$

(*c*) $PE_n \propto \frac{1}{m_\pi}\left(\frac{n^2}{Z^2}\right)$ (*d*) $PE_n \propto \frac{1}{m_\pi}\left(\frac{Z^2}{n^2}\right)$

15. Number of waves made by the pion when orbiting in third excitation state are:

(*a*) 3 (*b*) 4

(*c*) $3Z^2$ (*d*) $4Z^2$

16. The longest wavelength radiation emitted in the emission spectrum when the pion de-excites from n = 3 to ground state lies in which of the following region?

(*a*) UV

(*b*) Visible

(*c*) Infra-Red

(*d*) Depends on Z^2

17. The wavelength (λ_n) of the pion orbiting in n^{th} stationary state is given by

(*a*) $\lambda_\pi \propto \frac{n}{m_\pi Z}$ (*b*) $\lambda_\pi \propto \frac{m_\pi n}{Z}$

(*c*) $\lambda_\pi \propto \frac{m_\pi Z}{n}$ (*d*) $\lambda_\pi \propto \frac{Z}{m_\pi n}$

> *"Resilience is not about avoiding stress but learning to thrive in it."*

ANSWER KEY

CONCEPT APPLICATION

1. (*a*) 2. (*b*) 3. (*c*) 4. (*b*) 5. (*a*) 6. (*d*) 7. (*b*) 8. (*c*) 9. (*a*) 10. (*b*)
11. (*a*) 12. (*a*) 13. (*c*) 14. (*b*) 15. (*b*) 16. (*a*) 17. (*d*) 18. (*c*) 19. (*d*) 20. (*c*)
21. (*b*) 22. (*b*) 23. (0.423Å) 24. (*c*) 25. (*a*) 26. (*d*) 27. (*a*) 28. (*b*) 29. (*b*)
30. (*a*) 31. (*c*) 32. (*d*) 33. (*a*)

SCHOOL LEVEL PROBLEMS

1. (*a*) 2. (*d*) 3. (*b*) 4. (*a*) 5. (*d*) 6. (*b*) 7. (*c*) 8. (*d*) 9. (*c*) 10. (*a*)
11. (*d*) 12. (*a*) 24. (*i*)-(*d*), (*ii*)-(*a*), (*iii*)-(*c*), (*iv*)-(*c*)

PRARAMBH (TOPICWISE)

1. (*a*) 2. (*c*) 3. (*b*) 4. (*d*) 5. (*c*) 6. (*d*) 7. (*c*) 8. (*b*) 9. (*a*) 10. (*d*)
11. (*d*) 12. (*c*) 13. (*a*) 14. (*a*) 15. (*d*) 16. (*c*) 17. (*c*) 18. (*c*) 19. (*d*) 20. (*c*)
21. (*a*) 22. (*b*) 23. (*a*) 24. (*a*) 25. (*b*) 26. (*a*) 27. (*b*) 28. (*b*) 29. (*c*) 30. (*b*)
31. (*c*) 32. (*a*) 33. (*d*) 34. (*c*) 35. (*c*) 36. (*c*) 37. (*b*) 38. (*c*) 39. (*d*) 40. (*d*)
41. (*c*) 42. (*c*) 43. (*c*) 44. (*a*) 45. (*b*) 46. (*c*) 47. (*d*) 48. (*d*) 49. (*a*) 50. (*b*)
51. (*c*) 52. (*d*) 53. (*a*) 54. (*d*) 55. (*b*) 56. (*b*) 57. (*a*) 58. (*b*) 59. (*b*) 60. (*b*)
61. (*d*) 62. (*c*) 63. (*a*) 64. (*c*) 65. (*c*) 66. (*c*) 67. (*b*) 68. (*d*) 69. (*d*) 70. (*b*)

PRABAL (JEE MAIN LEVEL)

1. (*a*) 2. (*c*) 3. (*d*) 4. (*c*) 5. (*a*) 6. (*a*) 7. (*b*) 8. (*b*) 9. (*d*) 10. (*c*)
11. (*b*) 12. (*d*) 13. (*c*) 14. (*a*) 15. (*c*) 16. (*d*) 17. (*b*) 18. (*b*) 19. (*c*) 20. (*d*)
21. (*b*) 22. (*d*) 23. (*c*) 24. (*d*) 25. (*c*) 26. (*c*) 27. (*c*) 28. (*b*) 29. (*d*) 30. (*b*)
31. (*d*) 32. (*b*) 33. (*c*) 34. (*b*) 35. (*c*) 36. [6] 37. [8] 38. [26] 39. [4] 40. [4]
41. [1240] 42. [31] 43. [12] 44. [5] 45. [90] 46. [97] 47. [1] 48. [4] 49. [3] 50. [17]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*b*) 2. (*d*) 3. (*c*) 4. (*c*) 5. (*a*) 6. (*a*) 7. (*c*) 8. (*a*) 9. (*b*) 10. (*d*)
11. (*b*) 12. (*c*) 13. (*a*) 14. (*a,b,c*) 15. (*a,b,c*) 16. (*a,b,c,d*) 17. (*a,b,c*) 18. (*a,b,c*) 19. (*a,c*) 20. (*b,c*)
21. (*a,b,c*) 22. (*a,b,c*) 23. (*a,c*) 24. (*b,c*) 25. (*a,c,d*) 26. (*b,c,d*) 27. (*a,b,c*) 28. (*c,d*) 29. (*a*) 30. (*b*)
31. (*c*) 32. (*d*) 33. (*c*) 34. (*b*) 35. (*a*) 36. (*a*) 37. (*c*) 38. (*d*) 39. [14] 40. [5]
41. [3] 42. [5] 43. [9] 44. [1] 45. [20] 46. [12] 47. [106] 48. [9] 49. [47] 50. [9]
51. [84] 52. [11] 53. [20] 54. [435] 55. [1667]

PYQ's (PAST YEAR QUESTIONS)

1. (*d*) 2. [2] 3. [4] 4. (*d*) 5. (*b*) 6. [494] 7. (*b*) 8. [5] 9. [1724] 10. (*b*)
11. [2] 12. (*c*) 13. [2] 14. (*c*) 15. (*d*) 16. (*c*) 17. [30] 18. (*c*) 19. [10] 20. [658]
21. [8] 22. [22] 23. [34] 24. (*a*) 25. (*b*) 26. [3155] 27. (*c*) 28. (*d*) 29. (*a*) 30. [30]
31. [–5246.49] 32. (*c*) 33. (*d*) 34. (*a*) 35. [58] 36. (*d*) 37. [548] 38. [58] 39. [16]
40. (*a*) 41. (*a*) 42. (*b*) 43. (*a*) 44. [4] 45. [6] 46. (*d*) 47. (*b*) 48. (*c*) 49. (*a*)
50. (*a,c*)

PW CHALLENGERS

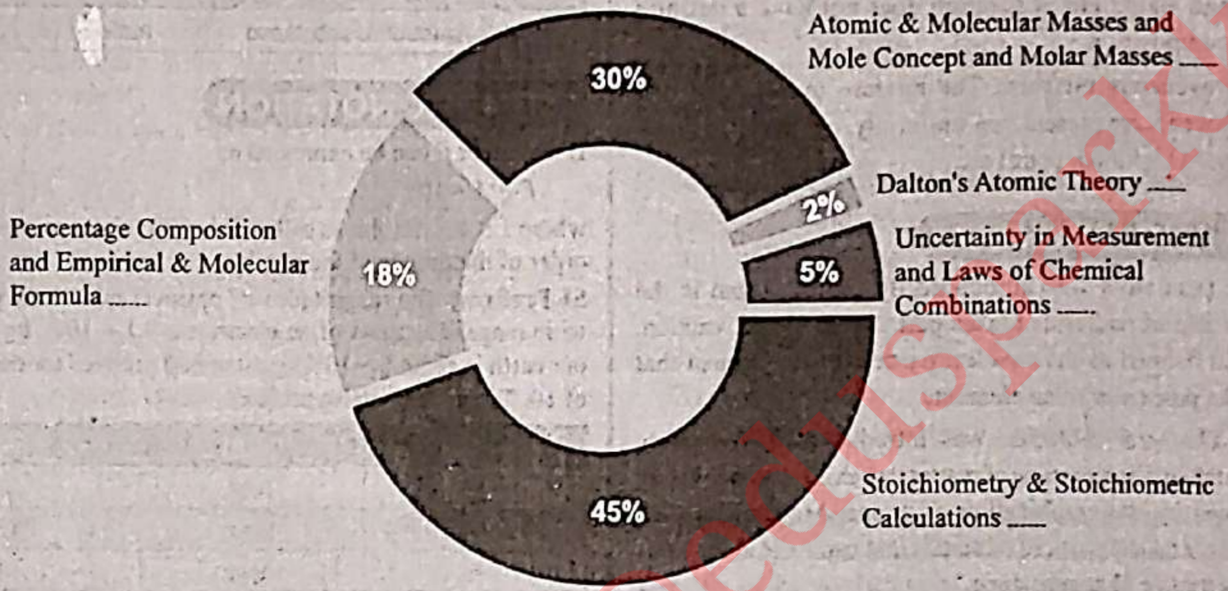
1. (*a*) 2. [300303] 3. [9] 4. [3] 5. [0.762] 6. [2.35] 7. (*c*) 8. (*d*) 9. (*c*)
10. (*a*) 11. (*b*) 12. (*c*) 13. (*d*) 14. (*b*) 15. (*b*) 16. (*d*) 17. (*a*)

CHAPTER

2

Some Basic Concepts of Chemistry

Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

MATTER

A substance which occupies space, possesses mass and can be felt by any one or more of the five senses is called matter.

Physical Classification of Matter

It is based on physical state under ordinary conditions of temperature and pressure.

(*a*) **Solid:** A substance is said to be solid if it possesses a definite volume and a definite shape, e.g. sugar, iron, gold, wood etc.

(*b*) **Liquid:** A substance is said to be liquid if it possesses a definite volume but not definite shape. They take up the shape of the container, e.g. water, milk, oil, mercury, alcohol etc.

(*c*) **Gas:** A substance is said to be gas if it neither possesses a definite volume nor a definite shape. This is because they fill up the whole container, e.g. Hydrogen (H_2), Oxygen (O_2), Carbon dioxide (CO_2) etc.

Chemical Classification of Matter

(*a*) **Pure Substance:** A material containing only one type of substance. Pure Substance can not be separated into simpler substance by physical method.

e.g.: Element = Na, Mg, Ca .... etc.

Compound = HCl, H_2O, CO_2, HNO_3 ....etc.

Pure substance is classified into two types:

(I) Element (II) Compound

(I) **Element:** The pure substance containing only one kind of atoms. It is classified into 3 types

(i) Metal → Zn, Cu, Hg, Ac, Sn, Pb etc.

(ii) Non-metal → N_2, O_2, Cl_2, Br_2, F_2, P_4, S_8 etc.

(iii) Metalloids → B, Si, As, Te etc.

(II) **Compound:** It is defined as pure substance containing more than one kind of elements or atoms which are combined together in a fixed proportion by weight and which can be decomposed into simpler substance by the suitable chemical method. The properties of a compound are completely different from those of its constituent element, e.g. HCl, H_2O, H_2SO_4, $HClO_4$, HNO_3 etc.

(*b*) **Mixture:** A material which contain more than one type of substances and which are mixed in any ratio by weight is called as mixture. The property of the mixture is the property of its components. The mixture can be separated by simple physical method.

Classification of Mixture

(*i*) **Homogeneous mixture:** The mixture, in which all the components are present uniformly is called as homogeneous mixture. Components of mixture are present in a single phase, e.g. Water + Salt, Water + Sugar, Water + alcohol.

Homogeneous substances are of two types:

(*a*) **Pure substances:** Substances which have definite and constant chemical composition are known as pure substances. For example, all elements and compounds are pure substances.

(*b*) **Solutions:** A homogenous mixture of two or more pure substances is known as a solution. For example, air, a mixture of NaCl and water, alcohol and water, etc. A solution does not have a definite composition.

(*ii*) **Heterogeneous mixture:** The mixture in which all the components are present non-uniformly, e.g. Water + Sand, Water + Oil, blood, petrol etc.

ATOMS AND MOLECULES

Atom: The term atom was introduced by Dalton. Atom is the smallest particle of matter that takes part in a chemical reaction. Atom is also defined as the smallest particle of an element that retains all the properties of an element.

Molecule: The term molecule was introduced by Avogadro. Molecule is the smallest particle of matter that exists independently and is formed by the combination of atoms. Molecule is also defined as the smallest particle of matter that can exist and retains all the properties of that substance.

Physical and Chemical Properties:

(*a*) **Physical Property:** The property which can be measured without changing the chemical composition of the substance is known as physical property like mass, volume, density, refractive index etc.

(*b*) **Chemical Property:** The property which can be evaluated at the cost of matter itself is known as chemical property. For example combustible nature of hydrogen gas can be verified by burning of hydrogen. The sweet taste of sugar by consuming it.

Physical Quantity and their Measurements in Chemistry

Physical Quantities

All quantities that can be measured are called physical quantities. eg. time, length, mass, force, work done, etc.

Fundamental Quantities

A set of physical quantities which are completely independent of each other but all other physical quantities can be expressed in terms of these physical quantities is called set of Fundamental Quantities. Fundamental units are those units which can neither be derived from one another nor they can be further resolved into any other units.

The Fundamental Quantities that are currently being accepted by the scientific community are mass, time, length, current, temperature, luminous intensity and amount of substance.

International System (SI) of Units

Table: SI base quantities and their units

S. No.	Physical quantity	unit	Symbol
1	Length	metre	m
2	Mass	kilogram	kg
3	Time	second	s
4	Temperature	kelvin	K
5	Electric current	ampere	A
6	Luminous Intensity	candela	cd
7	Amount of substance	mole	mol

SCIENTIFIC NOTATION

If a number P can be expressed as

$$P = A \times 10^x$$

where $1 \le A < 10$, this is called Scientific Notation and x is called order of magnitude of the number.

SI Prefixes: The magnitudes of physical quantities vary over a wide range. The mass of an electron is 9.1×10^{-31} kg and that of our earth is about 6×10^{24} kg. Standard prefixes for certain power of 10. Table shows these prefixes:

Power of 10	Prefix	Symbol
12	tera	T
9	giga	G
6	mega	M
3	kilo	k
2	hecto	h
1	deca	da
–1	deci	d
–2	centi	c
–3	milli	m
–6	micro	μ
–9	nano	n
–12	pico	p
–15	femto	f

SIGNIFICANT FIGURES OR DIGITS

The significant figures (SF) in a measurement are the figures or digits that are known with certainty plus one that is uncertain.

Larger the number of significant figures obtained in a measurement, greater is its accuracy and vice versa.

1. **Rules to find out the number of significant figures:**

   I Rule: All the non-zero digits are significant e.g. 1984 has 4 SF.

   II Rule: All the zeros between two non-zero digits are significant, e.g. 10806 has 5 SF.

   III Rule: All the zeros to the left of first non-zero digit are not significant, e.g.00108 has 3 SF.

   IV Rule: If the number is less than 1, zeros on the right of the decimal point but to the left of the first non-zero digit are not significant, e.g. 0.002308 has 4 SF.

V Rule: The trailing zeros (zeros to the right of the last non-zero digit) in a number with a decimal point are significant, e.g. 01.080 has 4 SF.

VI Rule: The trailing zeros in a number without a decimal point are not significant e.g. 010100 has 3 SF.

VII Rule: When the number is expressed in exponential form, the exponential term does not affect the number of S.F. For example in $x = 12.3 = 1.23 \times 10^1 = .123 \times 10^2 = 0.0123 \times 10^3 = 123 \times 10^{-1}$, each term has 3 SF only. **(Note:** It has 3 significant figure in each expression.)

2. **Rules for arithmetical operations with significant figures:**

I Rule: In addition or subtraction the number of decimal places in the result should be equal to the number of decimal places of that term in the operation which contain lesser number of decimal places, e.g. $12.587 - 12.5 = 0.087 \approx 0.1$ ($\because$ second term contain lesser i.e. one decimal place)

II Rule: In multiplication or division, the number of SF in the product or quotient is same as the smallest number of SF in any of the factors, e.g. $5.0 \times 0.125 = 0.625 = 0.62$

To avoid the confusion regarding the trailing zeros of the numbers without the decimal point the best way is to report every measurement in scientific notation (in the power of 10). In this notation every number is expressed in the form $a \times 10^b$, where a is the base number between 1 and 10 and b is any positive or negative exponent of 10. The base number a is written in decimal form with the decimal after the first digit. While counting the number of SF only base number is considered (Rule VII).

❖ The change in the unit of measurement of a quantity does not affect the number of SF. For example in 2.308 cm = 23.08 mm = 0.02308 m = 23080 µm each term has 4 SF.

ACCURACY AND PRECISION

The accuracy of a measurement is a measure of how close the measured value is to the true value of the quantity. Precision tells us to what resolution or limit the quantity is measured.

Illustration: Assertion: If the true value for a result is 2.00 g and a student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate.

Reason: Precision refers to the closeness of various measurements for the same quantity. Whereas, accuracy is the agreement of a particular value to the true value of the result.

In the light of the above statement, choose the correct answer from the options given below:

(*a*) Both Assertion and Reason are true and Reason is correct explanation of Assertion.

(*b*) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.

(*c*) Assertion is true but Reason is false.

(*d*) Assertion is false but Reason is true.

Sol. (*a*)

Illustration: Assertion: 100 has only one significant figure, but 100.0 has three significant figures and 100.0 has four significant figures.

Reason: Zeros at the end or right of a number are significant provided they are on the right side of the decimal point.

In the light of the above statement, choose the correct answer from the options given below:

(*a*) Both Assertion and Reason are true and Reason is correct explanation of Assertion.

(*b*) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.

(*c*) Assertion is true but Reason is false.

(*d*) Assertion is false but Reason is true.

Sol. (*a*)

Illustration: Assertion: All the zeros to the left of first non-zero digit are not significant.

Reason: Zeros at the end or right of a non-zero digit are significant provided they are on the right side of the decimal point.

In the light of the above statement, choose the correct answer from the options given below:

(*a*) Both Assertion and Reason are true and Reason is correct explanation of Assertion.

(*b*) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.

(*c*) Assertion is true but Reason is false.

(*d*) Assertion is false but Reason is true.

Sol. (*b*)

LAWS OF CHEMICAL COMBINATION

The law of conservation of mass (Law of Indestructibility of matter) According to this law, the mass can neither be created nor be destroyed in a balanced chemical reaction but one form is changed into another form. In a chemical change total mass remains conserved i.e., total mass before the reaction is always equal to total mass after the reaction.

$$H_2(g) \quad + \quad \frac{1}{2}O_2(g) \rightarrow \quad H_2O\,(\ell)$$

$$1 \text{ mole} \qquad \frac{1}{2} \text{ mole} \qquad 1 \text{ mole}$$

Mass before the reaction $= 1 \times 2 + \frac{1}{2} \times 32 = 18$ gm

Mass after the reaction $= 1 \times 18 = 18$ gm

[Total mass of reactants = Total mass of products + Mass of unreacted reactants]

Law of constant composition (definite proportions): All chemical compounds are found to have constant composition of elements irrespective of their method of preparation or sources. E.g. In H_2O, hydrogen & oxygen combine in 2 : 1 molar ratio, this ratio remains constant whether it is tap water, river water or seawater or produced by any chemical reaction.

Law of Multiple Proportions: When one element combines with the other element to form two or more different compounds, the mass of one element, which combines with a constant mass of the other bear a simple ratio to one another.

Nitrogen and oxygen combine to form five oxides: weights of oxygen which combine with the fixed weight of nitrogen in these oxides are calculated as under:

Oxide	Ratio of weights of nitrogen and oxygen
N_2O	28 : 16
NO	28 : 32
N_2O_3	28 : 48
N_2O_4	28 : 64
N_2O_5	28 : 80

Number of parts by weight of oxygen which combine with 14 parts by weight of nitrogen from the above are 8, 16, 24, 32 and 40 respectively. Their ratio is 1 : 2 : 3 : 4 : 5, which is a simple whole number ratio. Hence, the law of multiple proportion is illustrated.

ADVANCED LEARNING

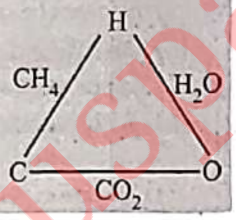
Law of Reciprocal Proportion: The ratio of the masses of two elements A and B which combine separately with a fixed mass of the third element C is either the same or some simple multiple of the ratio of the masses in which A and B combine directly with each other.

Like CH_4, CO_2 and H_2O

$CH_4 \rightarrow C : H = 12 : 4$

$CO_2 \rightarrow C : O = 12 : 32$

$H_2O \rightarrow H : O = 2 : 16$



Gay-Lussac's Law of Combining Volume: Gases combine in a simple whole number ratio of their volumes provided all measurements should be done at the same temperature and pressure.

$$\underset{1\ \text{vol.}}{H_2(g)} + \underset{1\ \text{vol.}}{Cl_2(g)} \rightarrow \underset{2\ \text{vol.}}{2HCl}$$

Avogadro's hypothesis: Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressure condition.

S.T.P. (Standard Temperature and Pressure) Temperature = 0°C or 273 K, Pressure = 1 atm = 760 mm of Hg.

Volume of one mole of gas at STP is found to be experimentally equal to 22.4 litres which is known as molar volume.

- Measuring the volume is equivalent to counting the number of molecules of the gas.

Train Your Brain

Example 1: A 15.9 g sample of sodium carbonate is added to a solution of acetic acid weighing 20.0 g. The two substances react, releasing carbon dioxide gas to the atmosphere. After reaction, the contents of the reaction vessel weigh 29.3 g. What is the mass of carbon dioxide given off during the reaction?

Sol. The total mass of reactants taken = 15.9 + 20.0 = 35.9 gm. From the conservation of mass, the final mass of the contents of the vessel should also be 35.9 gm. But it is only 29.3 gm. The difference is due to the mass of released carbon dioxide gas. Hence, the mass of carbon dioxide gas released = 35.9 – 29.3 = 6.6 gm

Example 2: The following are the results of analysis of two samples of the same or two different compounds of phosphorus and chlorine. From these results, decide whether the two samples are from the same or different compounds. Also state the law, which will be obeyed by the given samples.

	Amount of P	Amount of *Cl*
Compound A	1.156 gm	3.971 gm
Compound B	1.542 gm	5.297 gm

Sol. The mass ratio of phosphorus and chlorine in compound A, $m_P : m_{Cl} = 1.156 : 3.971 = 0.2911 : 1.000$

The mass ratio of phosphorus and chlorine in compound B, $m_P : m_{Cl} = 1.542 : 5.297 = 0.2911 : 1.000$

As the mass ratio is same, both the compounds are **same** and the samples obey the **law of definite proportion.**

Example 3: 2.5 ml of a gaseous hydrocarbon exactly requires 12.5 ml oxygen for complete combustion and produces 7.5 ml carbon dioxide and 10.0 ml water vapour. All the volumes are measured at the same pressure and temperature. Show that the data illustrates Gay Lussac's law of volume combination.

Sol. $V_{\text{hydrocarbon}} : V_{\text{oxygen}} : V_{\text{carbon dioxide}} : V_{\text{water vapour}}$

$= 2.5 : 12.5 : 7.5 : 10.0$

$= 1 : 5 : 3 : 4$ (simple whole no. ratio)

Hence, the data is according to the **law of volume combination.**

Concept Application

1. A sample of pure carbon dioxide, irrespective of its source contains 27.27% carbon and 72.73% oxygen. The data support:
   (*a*) Law of constant composition.
   (*b*) Law of conservation of mass.
   (*c*) Law of reciprocal proportions.
   (*d*) Law of multiple proportions.
2. The percentage of hydrogen in water and hydrogen peroxide is 11.1 and 5.9 respectively. These figures illustrate:
   (*a*) Law of multiple proportions.
   (*b*) Law of conservation of mass.
   (*c*) Law of constant proportions.
   (*d*) Law of combining volumes.
3. 1.0 g of an oxide of A contained 0.5 g of A. 4.0 g of another oxide of A contained 1.6 g of A. The data indicate the law of:
   (*a*) Reciprocal proportions.
   (*b*) Constant proportions.
   (*c*) Conservation of energy.
   (*d*) Multiple proportions.
4. Carbon is found to form two oxides which contain 42.9% & 27.3% of carbon respectively show that these figures shows the
   (*a*) Law of multiple proportion
   (*b*) Law of definite proportion
   (*c*) Law of mass conservation
   (*d*) All of these

ATOMIC MASS & MOLECULAR MASS

Relative Atomic Mass: One of the most important concept from Dalton's atomic theory was that of relative atomic mass or relative atomic weight. This is done by expressing mass of one atom with respect to a fixed standard. Dalton used hydrogen as the standard (H = 1). Later on oxygen (O = 16) replaced hydrogen as the reference.

- The present standard unit which was adopted internationally in 1961, is based on the mass of one carbon-12 isotopic atom, taken as exactly 12.000 u (amu).

  Relative atomic mass (R.A.M)

$$= \frac{\text{Mass of one atom of an element}}{\frac{1}{12} \times \text{Mass of one } C^{12} \text{ atom}}$$

Atomic Mass Unit (or amu): The atomic mass unit (amu) is equal to $\left(\frac{1}{12}\right)^{th}$ of mass of one atom of carbon-12 isotope.

$$\therefore \quad 1 \text{ amu} = \frac{1}{12} \times \text{mass of one } C^{12} \text{ isotopic atom}$$

$$\simeq \text{mass of one nucleon in } C^{12} \text{ atom.}$$

1 amu = 1.66×10^{-24} gm or 1.66×10^{-27} kg

- Today, amu has been replaced by 'u' which is known as unified atomic mass
- **One amu is also called One Dalton (Da).**
- Atomic mass = R.A.M × 1 amu

- Relative atomic mass indicates the number of nucleons present in the atom.

Average / Mean Atomic Mass

The weighted average of the isotopic masses of the element's naturally occurring isotopes.

Mathematically, average atomic mass of X (A_x)

$$= \frac{a_1x_1 + a_2x_2 + \ldots.. + a_nx_n}{100}$$

Where:

a_1, a_2, a_3 .... atomic mass of isotopes.

and x_1, x_2, x_3 .... mole% or % of natural abundance of isotopes.

Key Note

○ Atomic weights of many elements are not whole numbers due to the presence of stable isotopes.

○ The number of atoms of a particular isotope present in 100 atoms of a natural sample of that element is called its relative abundance which always remains constant for a given element.

○ Shortcut for % determination if average atomic weight is given for X having isotopes XA & XB.

$$\% \text{ of XA} = \left| \frac{\text{Average atomic weight} - \text{wt of } X^B}{\text{difference in weight of } X^A \ \& \ X^B} \right| \times 100$$

Illustration: Naturally occurring chlorine is 75% Cl^{35} which has an atomic mass of 35 amu and 25% Cl^{37} which has a mass of 37 amu. Calculate the average atomic mass of chlorine:

(*a*) 35.5amu (*b*) 36.5amu (*c*) 71amu (*d*) 72amu

Sol. (*a*) Average atomic mass

$$= \frac{(\% \text{ of I isotope}) \times (\text{its A.M}) + (\% \text{ of II isotope}) \times (\text{its A.M.})}{100}$$

$$= \frac{75 \times 35 + 25 \times 37}{100} = 35.5 \text{ amu}$$

Relative molecular mass:

$$= \frac{\textbf{mass of one molecule of the substance}}{\frac{1}{12} \times \textbf{mass of one } C^{12} - \textbf{atom}}$$

- Molecular mass = Relative molecular mass × 1 amu

Mean Molar Mass or Molecular Mass

The average molar mass of the different substance present in the container $= \frac{n_1M_1 + n_2M_2 + \ldots..n_nM_n}{n_1 + n_2 + \ldots.n_n}$.

Where:

M_1, M_2, M_3 .... are molar masses.

n_1, n_2, n_3 .... are moles of substances.

Formula Mass

The formula mass of a substance is defined as the sum of the atomic masses of constituent atoms in an ionic compound. This is generally used for ionic compounds which do not contain discrete molecules, but ions as their constituent units.

For example: Formula mass of NaCl is:

Formula mass = mass of sodium atom + mass of chlorine atom

= (23 + 35.5) u = 58.5 u

Illustration: The molar composition of polluted air is as follows:

Gas	At. wt.	mole percentage composition
Oxygen	16	16%
Nitrogen	14	80%
Carbon dioxide	-	03%
Sulphur dioxide	-	01%

What is the average molecular weight of the given polluted air? (Given, atomic weights of C and S are 12 and 32 respectively.

Sol. $M_{avg} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$ Here $\sum_{j=1}^{j=n} n_j = 100$

$$\therefore M_{avg} = \frac{16 \times 32 + 80 \times 28 + 44 \times 3 + 64 \times 1}{100}$$

$$= \frac{512 + 2240 + 132 + 64}{100} = \frac{2948}{100} = 29.48 \text{ Ans.}$$

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Example 4: Find the relative atomic mass of 'O' atom and its atomic mass.

Sol. The number of nucleons present in 'O' atom is 16.

$\therefore$ Relative atomic mass of 'O' atom = 16.

Atomic mass = R.A.M × 1 amu = 16 × 1 amu = 16 amu

Example 5: The weight of one atom of uranium is 235 amu. Its actual weight in g is:

Sol. $235 \times 1.67 \times 10^{-24}$ g

$= 3.95 \times 10^{-22}$ g

Concept Application

5. The Relative molecular mass of ammonia is:
   (*a*) 17 (*b*) 22 (*c*) 28 (*d*) 44
6. The mass of an atom of sodium is:
   (*a*) 23 amu (*b*) 23gm
   (*c*) 46 amu (*d*) 12 amu
7. The atomic mass & molecular mass of hydrogen is:
   (*a*) 1amu & 2amu (*b*) 2 amu & 4 amu
   (*c*) 3amu & 6amu (*d*) 4 amu & 8 amu
8. One 'u' stands for the
   (*a*) mass of an atom of carbon-12 atom.
   (*b*) 1/12th of mass of carbon-12.
   (*c*) 1/12th of mass of hydrogen atom.
   (*d*) mass of one atom of any of the element.
9. Mass of 1 amu in g is equal to:
   (*a*) 1.66×10^{24} g (*b*) 1.66×10^{-24} g
   (*c*) 1.008 g (*d*) 9.1×10^{-28} g

MOLE CONCEPT

Mole

Mole is a counting unit mostly used for microscopic particles and is defined as follows:

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg (or 12 gm) of the carbon-12 isotope.

From mass spectrometer we found that there are 6.022×10^{23} atoms present in 12 gm of C^{12} isotope.

The number of entities in 1 mol is so important that it is given a separate name and symbol known as Avogadro constant denoted by N_A. i.e., on the whole we can say that 1 mole is the collection of 6.022×10^{23} entities. Here entities may represent atoms, ions, molecules or even pens, chair, paper etc but as this number (N_A) is very large therefore it is significant only for very micro-particles.

Illustration: Chlorophyll, the green colouring material of plants contains 3.68 % of magnesium by mass. Calculate the number of magnesium atom in 5.00 g of the complex.

Sol. Mass of magnesium in 5.0 g of complex

$$= \frac{3.68}{100} \times 5.00 = 0.184 \text{ g}$$

Atomic mass of magnesium = 24

24 g of magnesium contain = 6.022×10^{23} atoms

0.184 g of magnesium would contain $= \dfrac{6.022 \times 10^{23}}{24} \times 0.184$

$= 4.617 \times 10^{21}$

Therefore, 5.00 g of the given complex would contain 4.617×10^{21} atoms of magnesium.

How Big is a Mole?

Amount of water in world's oceans (litres)
Age of earth (seconds)
Population of earth
Avogadro's number 602,200,000,000,000,000,000,000
Distance from earth to sun (centimeters)

- In modern practice gram-atom and gram-molecule are termed as mole.

Gram Atomic Mass: The atomic mass of an element expressed in gram is called gram atomic mass of the element.

or

It is also defined as mass of 6.022×10^{23} atoms.

or

It is also defined as the mass of one mole atoms.

Eg:

Element	R.A.M. (Relative Atomic Mass)	Atomic mass (mass of one atom)	Gram Atomic mass/weight
N	14	14 amu	14 gm
He	4	4 amu	4 gm
C	12	12 amu	12 gm

For example, for oxygen atom: Atomic mass of 'O' atom = mass of one 'O' atom = 16 amu

Gram atomic mass = mass of 6.022×10^{23} 'O' atoms

$= 16 \text{ amu} \times 6.022 \times 10^{23}$

$= 16 \times 1.66 \times 10^{-24} \text{ g} \times 6.022 \times 10^{23} = 16 \text{ g}$

$(\because 1.66 \times 10^{-24} \times 6.022 \times 10^{23} \simeq 1)$

Gram Molecular Mass: The molecular mass of a compound expressed in gram is called the gram-molecular mass of the compound.

or

It is also defined as mass of 6.022×10^{23} molecules.

or

It is also defined as the mass of one mole molecules.

For example, for 'O_2' molecule: Molecular mass of 'O_2' molecule

= mass of one 'O_2' molecule

= 2 × mass of one 'O' atom = 2 × 16 amu = 32 amu

Gram molecular mass = mass of 6.022×10^{23} 'O_2' molecules

$= 32 \text{ amu} \times 6.022 \times 10^{23}$

$= 32 \times 1.66 \times 10^{-24} \text{ gm} \times 6.022 \times 10^{23} = 32 \text{ gm}$

RELATIONSHIP BETWEEN GRAM AND AMU

$1 \text{ amu} = \dfrac{1}{12}$ of wt. of one C^{12} atom.

For carbon (C^{12}) atom, 1 mole C = 12 gm = 6.022×10^{23} atoms

wt. of 6.022×10^{23} C^{12} atoms = 12 gm

wt. of 1 atom of $C^{12} = \dfrac{12}{N_A}$ gm

(N_A → Avogadro's number = 6.022×10^{23}) .

$1 \text{ amu} = \frac{1}{12}$ of wt. of one C^{12} atom $= \frac{1}{12} \times \frac{12}{N_A}$ gm

$$\boxed{1 \text{ amu} = \frac{1}{N_A} \text{gm}}$$

METHODS OF CALCULATIONS OF MOLE

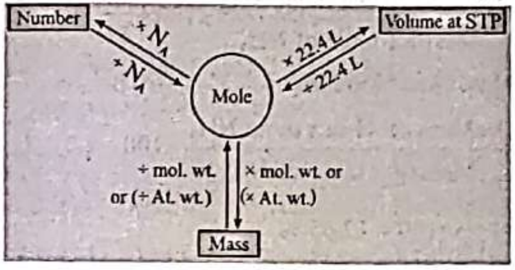
(*a*) If no. of particles of some species is given, then no. of moles $= \frac{\text{Given no. of particles}}{N_A}$.

(*b*) If weight of a given species is given, then no. of moles = $\frac{\text{Given wt.}}{\text{Atomic wt.}}$ (for atoms),

or $\frac{\text{Given wt.}}{\text{Molecular wt.}}$ (for molecules)

(*c*) If volume of a gas is given along with its temperature (T) and pressure (P) use $n = \frac{PV}{RT}$ (assuming gas to be ideal) where R = 0.0821 lit-atm/mol–K (when P is in atmosphere and V is in litre.)

Y-map: Interconversion of mole - volume, mass and number of particles:



ATOMICITY

It is equal to number of atoms present in one molecule. For example atomicity of H_2, CO_2, O_3, CCl_4, respectively.

DENSITY

For Liquids and Solids,

(*a*) Absolute density

$$\text{Absolute density} = \frac{\text{Mass}}{\text{Volume}}$$

(*b*) Relative density

$$\text{Relative density} = \frac{\text{Density of substance}}{\text{Density of standard substance}}$$

$$\text{e.g., Specific gravity} = \frac{\text{Density of substance}}{\text{Density of } H_2O \text{ at } 4°C}$$

For Gases:

$$\text{Absolute density (mass / volume)} = \frac{PM}{RT}$$

where P is pressure of gas, M = mol. wt. of gas, R is the gas constant, T is the temperature.

Vapour density: It is defined only for gas.

It is a density of gas with respect to H_2 gas at same temperature & pressure.

$$\therefore \text{V.D.} = \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas}/RT}{PM_{H_2}/RT} = \frac{M_{gas}}{M_{H_2}} = \frac{M}{2} \quad \boxed{\text{V.D.} = \frac{M}{2}}$$

Key Note

- ○ 1 g O, 1 g O_2, 1 g O_3 each have same number of oxygen atoms.
- ○ Density of liquid water at 4°C is 1 g/mL = 1 g/cc = 10^3 kg/m^3

Train Your Brain

Example 6: Total number of atoms of all elements present in 1 mole of ammonium dichromate is?

(*a*) 14 (*b*) 19
(*c*) 6×10^{23} (*d*) 114×10^{23}

Sol. (*d*) $(NH_4)_2Cr_2O_7 = 19 \times 6.022 \times 10^{23} \approx 114 \times 10^{23}$ atoms.

Example 7: How many atoms of oxygen are there in 16 g of oxygen?

(*a*) 2 N_A (*b*) N_A (*c*) 1.5 N_A (*d*) 4 N_A

Sol. (*b*) Let x atoms of oxygen are present

$$\text{So, } 16 \times 1.66 \times 10^{-24} \times x = 16 \text{ g} \Rightarrow x = \frac{1}{1.66 \times 10^{-24}} = N_A$$

Example 8: Calculate the volume in litres of 20 g hydrogen gas at STP.

(*a*) 2.24 L (*b*) 22.4 L
(*c*) 224 L (*d*) 4.48 L

Sol. (*b*) No. of moles of hydrogen gas $= \frac{\text{Mass}}{\text{Molecular mass}}$

$$= \frac{20 \text{ gm}}{2 \text{ gm}} = 10 \text{ mol}$$

Volume of hydrogen gas at STP = 10 × 22.4 L

Example 9: The number of atoms contained in 11.2 L of SO_2 at S.T.P. are:

(*a*) $3/2 \times 6.022 \times 10^{23}$ (*b*) $2 \times 6.022 \times 10^{23}$
(*c*) 6.022×10^{23} (*d*) $4 \times 6.022 \times 10^{23}$

Sol. (*a*) 22.4 litre gas has = 1 mole

$$1 \text{ litre gas has} = \frac{1}{22.4} \times 11.2 = \frac{1}{2} \text{ mole of molecules}$$

$$= 3 \times \frac{1}{2} \text{ mole of atoms} = \frac{3}{2} \times 6.022 \times 10^{23} \text{ atoms}$$

Example 10: 7.5 litre of the particular gas at S.T.P. weighs 16 gram. What is the V.D. of gas?

Sol. Moles at S.T.P. $= \frac{7.5}{22.4} = \frac{16}{M}$

$$M = 48 \text{ gram; V.D.} = \frac{48}{2} = 24.$$

Example 11: Find the vapour density of $CO_2(g)$ with respect to $N_2O(g)$.

Sol. $\text{V.D.} = \frac{\text{M.wt. of } CO_2}{\text{M.wt. of } N_2O} = \frac{44}{44} = 1$

Example 12: Find the vapour density of N_2O_5.

Sol. $\text{V.D.} = \frac{\text{Mol. wt. of } N_2O_5}{2} = \frac{108}{2} = 54$.

Concept Application

10. The number of electrons present in 1 mol of methane molecule are:
    (*a*) 6.022×10^{25} (*b*) 6.022×10^{24}
    (*c*) 6.022×10^{23} (*d*) 6.022×10^{22}
11. The mass of one molecule of water is approximately:
    (*a*) 3×10^{-23} g (*b*) 18 g
    (*c*) 1.5×10^{-23} g (*d*) 4.5×10^{-23} g
12. The molar mass of ferrous sulphate ($FeSO_4.7H_2O$) is:
    (*a*) 152 gm (*b*) 278 gm
    (*c*) 137 gm (*d*) None of these
13. The vapour density of carbon dioxide is:
    (*a*) 44 (*b*) 32 (*c*) 22 (*d*) 12
14. The density of air is 0.001293 g/cm³ at STP. Identify which of the following statement is correct?
    (*a*) Vapour density is 12.72.
    (*b*) Molecular weight is 28.96.
    (*c*) Vapour density is 0.001293 g/cm³.
    (*d*) Vapour density and molecular weight cannot be determined.

ELEMENTAL ANALYSIS

For n mole of a compound ($C_3H_7O_2$);

Moles of C = 3n
Moles of H = 7n
Moles of O = 2n

PERCENTAGE FORMULAE COMPOSITION

% of element in a compound

$$= \frac{\text{Atomic weight of element} \times \text{Number of atom of that element in one molecule} \times 100}{\text{Total molecular weight of compound}}$$

Here we are going to find out the percentage of each element in the compound by knowing the molecular formula of compound.

EMPIRICAL AND MOLECULAR FORMULA

We have just seen that knowing the molecular formula of the compound, we can calculate percentage composition of the elements. Conversely, if we know the percentage composition of the elements initially, we can calculate the relative number of atoms of each element in the molecules of the compound. This gives us the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can easily be determined.

An empirical formula represents the simplest whole number ratio of various atoms present in a compound.

The molecular formula gives the actual number of atoms of each element in a molecule. The molecular formula shows the exact number of different types of atoms present in a molecule of a compound. The molecular formula is an integral multiple of the empirical formula.

i.e. Molecular formula = Empirical formula × n

$$\text{where } n = \frac{\text{Molecular Formula Mass}}{\text{Empirical Formula Mass}}$$

- ❖ If sum of mass percent of all elements is less than 100 then difference is due to oxygen.
- ❖ $\text{Mass \% of C} = \frac{12}{44} \times \frac{m_{CO_2}}{m_{compound}} \times 100$
- ❖ $\text{Mass \% of H} = \frac{2}{18} \times \frac{m_{H_2O}}{m_{compound}} \times 100$

Train Your Brain

Example 13: Every molecule of ammonia always has formula NH_3 irrespective of method of preparation or sources. i.e. 1 mole of ammonia always contains 1 mol of N and 3 mole of H. In other words 17 gm of NH_3 always contains 14 gm of N and 3 gm of H. Now find out % of each element in the compound.

Sol. Mass % of N in NH_3 =

$$\frac{\text{Mass of N in 1 mole } NH_3}{\text{Mass of 1 mole of } NH_3} \times 100 = \frac{14}{17} \times 100 = 82.35\%$$

Mass % of H in NH_3 =

$$\frac{3 \times \text{Mass of H in 1 mole } NH_3}{\text{Mass of 1 mole of } NH_3} \times 100$$

$$= \frac{3}{17} \times 100 = 17.65\ \%$$

Example 14: Acetylene and benzene both have the empirical formula CH. The molecular masses of acetylene and benzene are 26 and 78 respectively. Deduce their molecular formulae.

Sol. ∵ Empirical Formula is CH

Step-1: The empirical formula of the compound is CH

∴ Empirical formula mass = (1 × 12) + 1 = 13.

Molecular mass = 26

Step-2: To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{26}{13} = 2$$

Step-3: To calculate the molecular formula of the Compound.

Molecular formula = n × (Empirical formula of the compound) = 2 × CH = C_2H_2

Thus the molecular formula is C_2H_2

Similarly for benzene

To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78}{13} = 6.$$

Thus the molecular formula is 6 × CH = C_6H_6

Example 15: An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition.

$C = 40.684\%$; $H = 5.085\%$ and $O = 54.228\%$

The molecular weight of the compound is 118. Calculate the molecular formula of the compound.

(*a*) $C_4H_6O_4$ (*b*) $C_2H_3O_2$

(*c*) $C_2H_4O_2$ (*d*) $C_4H_6O_8$

Sol. (*a*) **Step-1:** To calculate the empirical formula of the compound.

Element	Symbol	Percentage of element	At. mass of element	Relative no of atoms = $\frac{\text{Percentage}}{\text{At. mass}}$	Simplest atomic ratio	Simplest whole no. atomic ratio
Carbon	C	40.684	12	$\frac{40.684}{12} = 3.390$	$\frac{3.390}{3.389} = 1$	2
Hydrogen	H	5.085	1	$\frac{5.085}{1} = 5.085$	$\frac{5.085}{3.389} = 1.5$	3
Oxygen	O	54.228	16	$\frac{54.228}{16} = 3.389$	$\frac{3.389}{3.389} = 1$	2

$\therefore$ Empirical Formula is $C_2H_3O_2$

Step-2: To calculate the empirical formula mass.

The empirical formula mass of the compound is $12 \times 2 + 3 \times 1 + 16 \times 2 = 59$.

Step-3: To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$$

Step-4: To calculate the molecular formula of the salt.

Molecular formula = n × (Empirical formula)

$= 2 \times C_2H_3O_2 = C_4H_6O_4$

Thus the molecular formula is $C_4H_6O_4$

Example 16: Acetylene & butene have empirical formula CH & CH_2 respectively. The molecular mass of acetylene and butene are 26 & 56 respectively. Deduce their molecular formula.

Sol.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

For Acetylene : $n = \frac{26}{13} = 2$

$\therefore$ Molecular formula $= C_2H_2$

For Butene: $n = \frac{56}{14} = 4$

$\therefore$ Molecular formula $= C_4H_8$

Example 17: An oxide of nitrogen gave the following percentage composition by mass:

$N = 25.94$ and $O = 74.06$

Calculate the empirical formula of the compound.

(*a*) NO_2 (*b*) N_2O_4 (*c*) N_2O_5 (*d*) N_2O

Sol. (*c*)

Element	%/Atomic mass	divide by smallest ratio	Simple integer ratio
N	$\frac{25.94}{14} = 1.85$	$\frac{1.85}{1.85} = 1$	2
O	$\frac{74.06}{16} = 4.63$	$\frac{4.63}{1.85} = 2.5$	5

So empirical formula is N_2O_5.

Concept Application

15. A compound contains 25% hydrogen and 75% carbon by mass. Determine the empirical formula of the compound.

(*a*) CH_4 (*b*) C_2H_6

(*c*) C_3H_8 (*d*) C_2H_2

16. The empirical formula of a compound of molecular mass 120 u is CH_2O. The molecular formula of the compound is:

(*a*) $C_2H_4O_2$ (*b*) $C_4H_8O_4$

(*c*) $C_3H_5C_3$ (*d*) All of these

17. Calculate the molecular formula of compound which contains 20% Ca and 80% Br (by wt.) if molecular weight of compound is 200 u. (Atomic wt. Ca = 40. Br = 80)

(*a*) $Ca_{1/2}Br$ (*b*) $CaBr_2$

(*c*) CaBr (*d*) Ca_2Br

CONCENTRATION OF SOLUTION

Concentration of a solution can be expressed in any of the following ways.

(*i*) **% by wt.:** Amount of solute (in g) dissolved in 100 gm of solution.

4.9% H_2SO_4 by wt.

⇒ 100 gm of solution contains 4.9 gm of H_2SO_4.

(*ii*) **% by volume:** Volume of solute (in ml) dissolved in 100 ml of solution.

x% H_2SO_4 by volume

⇒ 100 ml of solution contains x ml H_2SO_4.

(*iii*) **% wt. by volume:** wt. of solute (in g) present in 100 ml of solution.

CONCENTRATION TERMS

Molarity (M): No. of moles of solute present in 1000 ml of solution.

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$$

Molality (m): No. of moles of solute present in 1000 gm of solvent.

$$m = \frac{\text{Moles of solute}}{\text{wt. of solvent in kg}}$$

Mole fraction: The mole fraction of a particular component in a solution is defined as the number of moles of that component per mole of solution.

If a solution has n_A mole of A & n_B mole of B.

$$\text{mole fraction of A } (X_A) = \frac{n_A}{n_A + n_B}$$

$$\text{mole fraction of B } (X_B) = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

Parts per million (ppm):

$$= \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

CONVERSION OF CONCENTRATION TERMS

1. **Molarity and % solute by mass:** Let d = density of solution in g/mL and let it contains x% (w/w) solute by mass. $\mathbf{M = \frac{x \times d \times 10}{m_A}}$

> - Specific gravity has no units and its numerical value equals density in g/mL.

2. **Molality and mole fraction:** Consider a binary solution consisting of two components A (Solute) and B (Solvent).

Let X_A & X_B are the mole fraction of A & B respectively.

$$X_A = \frac{n_A}{n_A + n_B}, \quad X_B = \frac{n_B}{n_A + n_B}$$

If molality of solution be m then:

$$m = \frac{n_A}{\text{mass of solvent}} \times 1000 = \frac{n_A}{n_B \times M_B} \times 1000$$

where M_B is the molecular wt. of the solvent B.

$$m = \frac{X_A}{X_B} \times \frac{1000}{M_B} \Rightarrow m = \frac{\text{mole fraction of A}}{\text{mole fraction of B}} \times \frac{1000}{M_B}$$

$$\boxed{m = \frac{\text{mole fraction of solute}}{\text{mole fraction of solvent}} \times \frac{1000}{\text{molecular wt. of solvent}}}$$

3. **Mole fraction of solute into molarity of solution** $\mathbf{M = \frac{X_2 d \times 1000}{X_1 M_1 + M_2 X_2}}$

Mole fraction of solvent and solute are X_1 and X_2 so $X_1 + X_2 = 1$

Suppose total mole of solution is = 1 then mole of solute and solute and solvent are X_2 & X_1 respectively

weight of solute = X_2M_2, weight of solvent = X_1M_1

& total wt of solution = $X_1M_1 + X_2M_2$

$$\text{volume of solution} = \frac{X_1M_1 + X_2M_2}{d}\,\text{ml} = \frac{X_1M_1 + X_2M_2}{d \times 1000}\,\text{L}$$

$$\text{molarity (M)} = \frac{X_2 \times d \times 1000}{X_1M_1 + X_2M_2}$$

4. **Molarity into mole fraction X_2 = 1000M/ [1000d – MM_2]**

Molarity = M moles solute in 1000 ml of solution

So, moles of solute = M & mass of solution = d × 1000

wt. of solute = MM_2 & wt. of solvent = $1000d - MM_2$

Where M_2 is molar mass of solute

mole fraction of solute = $1000M / [1000d - MM_2]$

5. **Molality into mole fraction** $\mathbf{X_2 = \frac{mM_1}{1000 + mM_1}}$

Molality = moles of solute in 1000 gm of solvent = m

$$\text{moles of solvent} = \frac{1000}{M_1} \text{ where } M_1 \text{ is molar mass of solvent}$$

$$\text{mole fraction } X_2 = \frac{m}{\frac{1000}{M_1} + m} = \frac{mM_1}{1000 + mM_1}$$

6. **Molality into molarity** $\mathbf{M = \frac{md \times 1000}{1000 + mM_2}}$

Molality = m moles of solute in 1000 gm of solvent

mole of solute = m & weight of solute = mM_2

Weight of solution = $1000 + mM_2$

$$\text{volume of solution} = \frac{1000 + mM_2}{d}\,\text{mL} = \frac{1000 + mM_2}{d \times 1000}\,\text{L}$$

$$\text{molarity} = \frac{m \times d \times 1000}{1000 + mM_2}$$

7. **Molarity into Molality** $\mathbf{m = \frac{M \times 1000}{1000d - MM_2}}$

M_1 and M_2 are molar masses of solvent and solute.

Molarity = M mole of solute in 1000 ml of solution

moles of solute = M & weight of solute = MM_2

weight of solution = 1000d

mass of solvent = $1000d - MM_2$

$$\text{molality} = \frac{M \times 1000}{1000d - MM_2}$$

$$\text{on simplifying } \boxed{d = M\left[\frac{1}{m} + \frac{M_2}{1000}\right]}$$

DILUTION & MIXING OF TWO LIQUIDS

- Upon dilution no. of moles of solute remains constant. If a particular solution having volume V_1 mL and molarity M_1 is diluted upto volume V_2 mL.

  $M_1V_1 = M_2V_2$

  M_2 : final molarity

- If a solution having volume V_1 and molarity M_1 is mixed with another solution of same solute having volume V_2 & molarity M_2 then $M_1V_1 + M_2V_2 = MR\,(V_1 + V_2)$

$$MR = \text{Resultant molarity} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

Key Note

> ○ Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

- ○ No. of moles of solute = Molarity × volume of solution (in L)
- ○ No. of millimoles of solute = Molarity × volume of solution (in mL)
- ○ 1 mole = 1000 millimole
- ○ All those concentration terms which does not involve volume terms e.g., ppm, mass %, molality, mole fraction are independent of temperature of the solution.
- ○ For dilue aqueous solution, molarity = molality
- ○ Concentration of solids or pure liquids is constant. (C = n/V = d/M)

Train Your Brain

Example 18: 0.2 mole of HCl and 0.1 mole of barium chloride were dissolved in 0.5 L of water to produce solution. The molarity of the Cl^- ions is:

(*a*) 0.06 M (*b*) 0.09 M
(*c*) 0.12 M (*d*) 0.80 M

Sol. (*d*) $HCl \longrightarrow Cl^-$

0.2 mole

$BaCl_2 \longrightarrow 2\,Cl^-$

$2 \times 0.1 = 0.2$

Total moles of $Cl^- = 0.4 \Rightarrow M = \dfrac{w \times 1000}{m \times v}$

$$\text{Molarity} = \frac{0.4 \times 1000}{500} = 0.8 \quad \because \left(\frac{w}{m} = 0.4\right)$$

Example 19: 149 g of potassium chloride (KCl) is dissolved in 10 L of an aqueous solution. Determine the molarity of the solution. (K = 39, Cl = 35.5)

(*a*) 0.2 M (*b*) 0.4 M (*c*) 0.5 M (*d*) 2.2 M

Sol. (*a*) Molecular mass of KCl = 39 + 35.5 = 74.5 g

$$\therefore \text{ Moles of KCl} = \frac{149\text{ g}}{74.5\text{ g}} = 2$$

$$\therefore \text{ Molarity of the solution} = \frac{2}{10} = 0.2\text{M}$$

Example 20: 255 g of an aqueous solution contains 5 g of urea. What is the concentration of the solution in terms of molality? (Mol. wt. of urea = 60)

(*a*) 0.222 m (*b*) 0.333 m
(*c*) 2.22 m (*d*) 3.33 m

Sol. (*b*) Mass of urea = 5 g

Molecular mass of urea = 60

$$\text{Number of moles of urea} = \frac{5}{60} = 0.083$$

Mass of solvent = (255 – 5) = 250 g

∴ Molality of the solution

$$= \frac{\text{Number of moles of solute}}{\text{Mass of solvent in gram}} \times 1000$$

$$= \frac{0.083}{250} \times 1000 = 0.332\text{ m}$$

Example 21: 117 g NaCl is dissolved in 500 ml aqueous solution. Find the molarity of the solution.

$$\textbf{Sol. } \text{Molarity} = \frac{117/58.5}{500/1000} = 4\text{M}.$$

Example 22: Calculate the resultant molarity of following:

(*a*) 200 ml 1M HCl + 300 ml water

(*b*) 1500 ml 1M HCl + 18.25 g HCl

(*c*) 200 ml 1M HCl + 100 ml 0.5 M H_2SO_4

(*d*) 200 ml 1M HCl + 100 ml 0.5 M HCl

Sol. (*a*) $\text{Final molarity} = \dfrac{200 \times 1 + 0}{200 + 300} = 0.4\text{M}.$

(*b*) $\text{Final molarity} = \dfrac{1500 \times 1 + \dfrac{18.25 \times 1000}{36.5}}{1500} = 1.33\text{ M}$

(*c*) $\text{Final molarity of } H^+ = \dfrac{200 \times 1 + 100 \times 0.5 \times 2}{200 + 100} = 1\text{M}$

(*d*) $\text{Final molarity} = \dfrac{200 \times 1 + 100 \times 0.5}{200 + 100} = 0.83\text{M}.$

Example 23: 518 g of an aqueous solution contains 18 g of glucose (mol.wt. = 180). What is the molality of the solution?

Sol. wt. of solvent = 518 – 18 = 500 g.

$$\Rightarrow \text{So molarity} = \frac{18/180}{500/1000} = 0.2\text{M}$$

Example 24: 0.25 g of a substance is dissolved in 6.25 g of a solvent. Calculate the percentage amount of the substance in the solution.

Sol. Wt. of solution = 0.25 + 6.25 = 6.50

$$\text{So \% (w/w)} = \frac{0.25}{6.50} \times 100 = 3.8\%$$

Example 25: An aqueous solution is 1.33 molal in methanol. Determine the mole fraction of methanol & H_2O.

Sol. Molality

$$= \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent} \times \text{mol.wt. of solvent}} \times 1000$$

$$1.33 = \frac{X_A}{X_B \times M_B} \times 1000 ; \frac{1.33 \times 18}{1000} = \frac{X_A}{X_B} ; \frac{23.94}{1000} = \frac{X_A}{X_B}$$

$$\Rightarrow X_A = 0.02394\,X_B,\ X_A + X_B = 1 \Rightarrow 1.02394\,X_B = 1$$

$$X_B = \frac{1}{1.02394} = 0.98, X_A = 0.02$$

2nd Method: Let wt.-of solvent = 1000 gm,
molality = 1.33 means 1.33 moles of solute are present in 1000 g solvent

mole fraction of solute

$$= \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}},$$

$$= \frac{m}{m + \frac{1000}{18}} = \frac{1.33}{1.33 + (1000/18)}$$

Mole fraction of solute = 0.02

Mole fraction of solvent = 1 − 0.02 = 0.98

Concept Application

18. If 500 ml of 1 M solution of glucose is mixed with 500 ml of 1 M solution of glucose, final molarity of solution will be:

(*a*) 1 M (*b*) 0.5 M (*c*) 2 M (*d*) 1.5 M

19. The volume of water that must be added to a mixture of 250 ml of 0.6 M HCl and 750 ml of 0.2 M HCl to obtain 0.25 M solution of HCl is:

(*a*) 750 ml (*b*) 100 ml (*c*) 200 ml (*d*) 300 ml

20. The molarity of Cl^- in an aqueous solution which was (w/v) 2% NaCl, 4% $CaCl_2$ and 6% NH_4Cl will be:

(*a*) 0.342 (*b*) 0.721 (*c*) 1.12 (*d*) 2.18

21. 2M of 100 ml Na_2SO_4 is mixed with 3M of 100 ml NaCl solution and 1 M of 200 ml $CaCl_2$ solution. Then the ratio of the concentration of cation and anion.

(*a*) 1/2 (*b*) 2 (*c*) 1.5 (*d*) 1

22. Equal moles of H_2O and NaCl are present in a solution. Hence, molality of NaCl solution is :

(*a*) 0.55 (*b*) 55.5 (*c*) 1.00 (*d*) 0.18

23. Mole fraction of A in H_2O is 0.2. The molality of A in H_2O is:

(*a*) 13.9 (*b*) 15.5 (*c*) 14.5 (*d*) 16.8

24. What is the molarity of H_2SO_4 solution that has a density of 1.84 g/cc and contains 98% by mass of H_2SO_4? (Given atomic mass of S = 32)

(*a*) 4.18 M (*b*) 8.14M (*c*) 18.4 M (*d*) 18 M

25. The molarity of the solution containing 2.8% (mass/volume) solution of KOH is : (Given atomic mass of K = 39) is :

(*a*) 0.1 M (*b*) 0.5 M (*c*) 0.2 M (*d*) 1 M

STOICHIOMETRY BASED CONCEPT (PROBLEMS BASED ON CHEMICAL REACTION)

All chemical reaction are represented by chemical equations by using chemical formulae of reactants and products. Qualitatively a chemical equation simply describes what the reactants and products are. However, a balanced chemical equation gives us a lot of quantitative information mainly the molar ratio in which reactants combine and the molar ratio in which products are formed.

Example:

When potassium chlorate ($KClO_3$) is heated it gives potassium chloride (KCl) and oxygen (O_2).

$$KClO_3 \longrightarrow KCl + O_2 \text{ (unbalanced chemical equation)}$$

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \text{ (balanced chemical equation)}$$

Attributes of a balanced chemical equation:

(*a*) It contains an equal number of atoms of each element on both sides of equation.

(*b*) It should follow law of charge conservation on either side.

(*c*) Physical states of all the reagents should be included in brackets.

(*d*) All reagents should be written in their standard molecular forms (not as atoms)

(*e*) The coefficients give the relative molar ratios of each reagent.

Balancing a Chemical Equation

Many chemical equations can be balanced by trial and error. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

For Example:

Combustion reaction of C_2H_6 : $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$ (skeleton equation)

Balance carbon atoms: $C_2H_6 + O_2 \rightarrow 2CO_2 + H_2O$

Now balance hydrogen atoms: $C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$

Now balance oxygen atoms: $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

Always remember that subscripts in formula of reactants and products cannot be changed to balance an equation.

One of the most important aspects of a chemical equation is that when it is written in the balanced form, it gives quantitative relationships between the various reactants and products in terms of moles, masses, molecules and volumes.

Mole - Mole Analysis

This analysis is very much important for quantitative analysis point of view.

Consider the decomposition of $KClO_3$.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

In very first step of mole-mole analysis you should read the balanced chemical equation like **2 moles $KClO_3$ on decomposition gives you 2 moles KCl and 3 moles O_2** and from the stoichiometry of reaction we can write

$$\frac{\text{Moles of KClO}_3}{2} = \frac{\text{Moles of KCl}}{2} = \frac{\text{Moles of O}_2}{3}$$

Now for any general balanced chemical equation like

$$aA + bB \longrightarrow cC + dD$$

you can write.

$$\frac{\text{Moles of A reacted}}{a} = \frac{\text{Moles of B reacted}}{b}$$

$$= \frac{\text{Moles of C produced}}{c} = \frac{\text{Moles of D produced}}{d}$$

Further, a balanced chemical equation along with the quantitative information conveyed by it is given below:

$$\begin{array}{lllll}
CaCO_3 & + \; 2HCl & \longrightarrow CaCl_2 & + \; H_2O & + \; CO_2 \\
1\text{ Mole} & 2\text{ Mole} & 1\text{ Mole} & 1\text{ Mole} & 1\text{ Mole} \\
40+12+3\times16 & 2(1+35.5) & 40+2\times35.5 & 2\times1+16 & 12+2\times16 \\
= 100\text{ g} & = 73\text{ g} & = 111\text{ g} & = 18\text{ g} & = 44\text{ g or } 22.4\text{ L} \\
 & & & & \text{at STP}
\end{array}$$

Thus,

(*i*) 1 mole of calcium carbonate reacts with 2 moles of hydrochloric acid to give 1 mole of calcium chloride, 1 mole of water and 1 mole of carbon dioxide.

(*ii*) 100 g of calcium carbonate react with 73 g hydrochloric acid to give 111 g of calcium chloride, 18 g of water and 44 g (or 22.4 litres at STP) of carbon dioxide.

Stoichiometry:

$$\begin{array}{lll}
N_2 \quad + & 3H_2 & \rightarrow 2NH_3 \\
1\text{ mole} & 3\text{ mole} & 2\text{ mole} \\
22.4\text{ litre} & 3\times22.4\text{ litre} & 2\times22.4\text{ litre (at STP)} \\
1\text{ litre} & 3\text{ litre} & 2\text{ litre} \\
1000\text{ mL} & 3000\text{ mL} & 2000\text{ mL} \\
1\text{ mL} & 3\text{ mL} & 2\text{ mL} \\
28\text{ gm} & 6\text{ gm} & 34\text{ g}
\end{array}$$

(law of conservation of mass is followed).

- Mass can not be represented by stoichiometry.
- The quantitative information conveyed by a chemical equation helps in a number of calculations. The problems involving these calculations may be classified into the following different types:

Type (I) Mass - Mass Relationships i.e. mass of one of the reactants or products is given and the mass of some other reactant or product is to be calculated.

Mass - Mass Analysis

Consider the reaction $2KClO_3 \rightarrow 2KCl + 3O_2$

According to stoichiometry of the reaction

mass-mass ratio = 2 × 122.5 : 2 × 74.5 : 3 × 32

$$\text{or} \quad \frac{\text{Mass of KClO}_3}{\text{Mass of KCl}} = \frac{2\times122.5}{2\times74.5}$$

$$\frac{\text{Mass of KClO}_3}{\text{Mass of O}_2} = \frac{2\times122.5}{3\times32}$$

Illustration: Calculate the weight of iron which will be converted into its oxide by the action of 36 g of steam.

(Given : $3Fe + 4H_2O \longrightarrow Fe_3O_4 + H_2$)

Sol. Mole ratio of reaction suggests,

$$\frac{\text{Mole of Fe}}{\text{Mole of H}_2\text{O}} = \frac{3}{4}$$

$$\therefore \text{Mole of Fe} = \frac{3}{4} \times \text{mol of H}_2\text{O} = \frac{3}{4}\times\frac{36}{18} = \frac{3}{2}$$

$$\text{wt. of Fe} = \frac{3}{2} \times 56 = 84\text{ g}$$

Illustration: What amount of silver chloride is formed by the action of 5.850 g of sodium chloride on an excess of silver nitrate?

Sol. Writing the balanced equation for the reaction

$$\begin{array}{llll}
NaCl \quad + & AgNO_3 \longrightarrow & AgCl \quad + & NaNO_3 \\
1\text{ mol} & 1\text{ mol} & 1\text{ mol} & 1\text{ mol}
\end{array}$$

$$n_{NaCl} = \frac{\text{Weight}}{M_w} = \frac{5.85}{58.5} = 0.1\text{ mol}$$

$$\frac{\text{mole(NaCl)}}{\text{mole(AgCl)}} = \frac{1}{1}$$

$$\Rightarrow \text{mole (AgCl)} = 0.1 = \frac{\text{Weight}}{M_w} = \frac{\text{Weight}}{143.5}$$

$$\Rightarrow \text{weight} = 0.1 \times 143.5\text{ g} = 14.35\text{ g.}$$

Illustration: How much iron can be theoretically obtained in the reduction of 1 kg of Fe_2O_3?

Sol. Writing the balanced equation for the decomposition reaction. $Fe_2O_3 \rightarrow 2Fe + \frac{3}{2}O_2$

$$n_{Fe_2O_3} = \frac{\text{Weight}}{M_w} = \frac{1000}{160}\text{ mol}$$

$$\frac{\text{mole(Fe}_2\text{O}_3)}{\text{mole(Fe)}} = \frac{1}{2}$$

$$\Rightarrow \text{moles of Fe} = \frac{2\times1000}{160} = 12.5\text{ mol}$$

$$= \frac{\text{Weight}}{\text{Atomic weight}} = \frac{\text{Weight}}{56}$$

Weight of iron obtained = 12.5 × 56 g = 700 g

Type (II) Mass - Volume Relationships i.e. mass/volume of one of the reactants or products is given and the volume/mass of the other is to be calculated.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

Mass volume ratio =

2 × 122.5 g : 2 × 74.5 g : 3 × 22.4 L at STP

we can use two relation for volume of oxygen

$$\frac{\text{Mass of KClO}_3}{\text{Volume of O}_2\text{ at STP}} = \frac{2\times122.5\text{g}}{3\times22.4\text{L}} \quad \text{...(i)}$$

$$\text{and} \quad \frac{\text{Mass of KCl}}{\text{Volume of O}_2\text{ at STP}} = \frac{2\times74.5\text{g}}{3\times22.4\text{L}} \quad \text{...(ii)}$$

Illustration: How much marble of 90.5% purity would be required to prepare 10 litres of CO_2 at STP when the marble is acted upon by dilute HCl?

Sol. $\underset{100\text{ g}}{CaCO_3} + 2HCl \longrightarrow CaCl_2 + H_2O + \underset{22.4\text{litre}}{CO_2}$

22.4 L of CO_2 at STP will be obtained from 100 g of $CaCO_3$

∴ 10 L of CO_2 at STP will be obtained from pure

$$CaCO_3 = \frac{100}{22.4}\times10 = 44.64\text{ g}$$

$$\therefore \text{Impure marble required} = \frac{100}{90.5} \times 44.64 = 49.326\text{ g}$$

Illustration: At 100°C for complete combustion of 3g ethane the required volume of O_2 & produced volume of CO_2 at STP will be?

Sol. $2C_2H_6 \;+\; 7O_{2(g)} \;\rightarrow\; 4CO_{2(g)} \;+\; 6H_2O_{(g)}$

$\quad\;\; 2 \qquad\quad 7 \qquad\qquad 4 \qquad\qquad 6$

$$n_{C_2H_6} = \frac{\text{Weight}}{M_w} = \frac{3}{30} = \frac{1}{10} = 0.1 \text{ mol}$$

$\therefore$ Required moles of $O_2 = \frac{7}{2} \times 0.1 = 0.35$ mol.

Required Volume of O_2 at STP $= 0.35 \times 22.4 = 7.84$ L.

And produced moles of $CO_2 = \frac{4}{2} \times 0.1 = 0.2$ mol.

Volume of CO_2 obtained at STP $= 0.2 \times 22.4 = 4.48$ L.

Illustration: In the following reaction, if 10 g of H_2 is reacted with N_2, what will be the volume of NH_3 produced at STP?

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Sol. $N_2 \;+\; 3H_2 \;\longrightarrow\; 2NH_3$

$$n_{H_2} = \frac{\text{Weight}}{M_w} = \frac{10}{2} = 5 \text{ mol.}$$

Produced moles of $NH_3 = \frac{2}{3} \times 5 = \frac{10}{3}$.

Volume of NH_3 produced at STP $= \frac{10}{3} \times 22.4 = 74.67$ L

Type (III) Volume - Volume Relationships i.e. volume of one of the reactants or the products is given and the volume of the other is to be calculated.

Illustration: At 100°C for complete combustion of 1.12 litre of butane (C_4H_{10}), the produced volume of $H_2O(g)$ & CO_2 at STP will be.

Sol. $1 \qquad\quad 13/2 \qquad\qquad 4 \qquad\qquad 5$

$C_4H_{10(g)} + 13/2\; O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(g)}$

1.12 litre

Volume of $H_2O_{(g)}$ at STP $= 5 \times 1.12 = 5.6$ litre

Volume of $CO_{2(g)}$ at STP $= 4 \times 1.12 = 4.48$ litre

Illustration: At 25°C for complete combustion of 5 mole propane (C_3H_8), the required volume of O_2 at STP will be?

Sol. For C_3H_8, the combustion reaction is

$C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$

5 mol

Required moles of $O_2 = 5 \times 5 = 25 \text{ mol} = \frac{V}{22.4}$.

Volume of O_2 gas at STP (V) $= 25 \times 22.4 = 560$ L.

Illustration: 3 litre of mixture of propane (C_3H_8) & butane (C_4H_{10}) on complete combustion give 10 litre CO_2. Find the composition of the mixture.

Sol. Let the volume of propane in the mixture = x litre,

$\therefore$ The volume of butane in the mixture = (3 – x) litre

Now let us calculate the volume of CO_2 evolved with the help of chemical equation.

Step-I: Calculation of volume of CO_2 from x litre of propane.

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

x litre $\qquad\qquad$ 3x litre

Step-II: Calculation of volume of CO_2 from (3 – x) litre of butane. The combustion equation for butane is:

$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$

(3–x) litre $\qquad\qquad$ 4(3–x) litre

Step-III: Calculation of composition of the mixture.

Total volume of CO_2 formed in the step (I) and step (II) = [3x + 4(3 – x)] litre

But the volume of CO_2 actually formed = 10 litre

$3x + 4(3 - x) = 10$

or $3x + 12 - 4x = 10$ $\qquad$ or $\qquad$ $x = 2$ litre

$\therefore$ Volume of propane = x litre = 2 litre

$\therefore$ Volume of butane = (3 – x) litre = (3 – 2) = 1 litre

Train Your Brain

Example 26: Write a balanced chemical equation for the following reaction:

When ammonia (NH_3) decompose into nitrogen (N_2) gas & hydrogen (H_2) gas.

Sol. $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$ or $2NH_3 \rightarrow N_2 + 3H_2$

Example 27: When 170 g NH_3 (M =17) decomposes, how many grams of N_2 & H_2 is produced?

Sol. $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$

$$\frac{\text{moles of } NH_3}{1} = \frac{\text{moles of } N_2}{1/2} = \frac{\text{moles of } H_2}{3/2}$$

So, moles of $N_2 = \frac{1}{2} \times \frac{170}{17} = 5$

So, wt. of $N_2 = 5 \times 28 = 140$ g

Similarly moles of $H_2 = \frac{3}{2} \times \frac{170}{17} = 15$

So, wt. of $H_2 = 15 \times 2 = 30$ g.

Example 28: When 340 g NH_3 (M = 17) decomposes, how many litres of nitrogen gas is produced at STP?

(*a*) 2.24 L $\quad$ (*b*) 22.4 L $\quad$ (*c*) 224 L $\quad$ (*d*) None

Sol. (*c*) $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$

Moles of $NH_3 = \frac{340}{17} = 20$

So moles of $N_2 = \frac{1}{2} \times 20 = 10$

$\therefore$ Vol. of N_2 at STP $= 10 \times 22.4 = 224$ L.

Concept Application

26. If 1.5 moles of dioxygen combine with Al to form Al_2O_3, the weight of Al used in the reaction is:
(*a*) 27 g (*b*) 40.5 g (*c*) 54 g (*d*) 81 g

27. How many litres of CO_2 at STP will be formed when 0.01 mol of H_2SO_4 reacts with excess of Na_2CO_3?
$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$
(*a*) 22.4 L (*b*) 2.24 L (*c*) 0.224 L (*d*) 1.12L

28. How many moles of potassium chlorate need to be heated to produce 11.2 litre oxygen at S.T.P.?

$$KClO_3 \longrightarrow KCl + \frac{3}{2}O_2$$

(*a*) $\frac{1}{2}$mol (*b*) $\frac{1}{3}$mol
(*c*) $\frac{1}{4}$mol (*d*) $\frac{2}{3}$mol

LIMITING REAGENT (L.R.) CONCEPT

Quite often one of the reactants is present in larger amount than the other as required according to the balanced equation. The amount of the product formed then depends upon the reactant which has reacted completely. This reactant is called the limiting reactant. The excess of the other is left unreacted.

Limiting Reagent (L.R.): The reactant which is completely consumed in a reaction is called as L.R.

Calculation of Limiting Reagent:

(*a*) By calculating the required amount by the equation and comparing it with given amount. [Useful when only two reactant are there]

(*b*) By calculating amount of any one product obtained taking each reactant one by one irrespective of other reactants. The one giving least product is limiting reagent.

(*c*) Divide given moles of each reactant by their stoichiometric coefficient, the one with least ratio is limiting reagent. [Useful when number of reactants are more than two.]

Ex.	A +	2B ⟶	C +	2D
Given moles	3	9	0	0
	3 − 3	9 − 6		
	0	3	3	6

A is L.R.

Formula for checking L.R. =

$$\frac{\text{Given value (moles, volume, or molecules)}}{\text{Stoichiometry Coefficient}}$$

Least value indicate the L.R.

Ex. A B

$\frac{3}{1} = 3$ $\frac{9}{2} = 4.5$

3 < 4.5 So, A is L.R

PERCENTAGE YIELD

The percentage yield of product

$$= \frac{\text{Actual yield}}{\text{theoretical maximum yield}} \times 100$$

The actual amount of any limiting reagent consumed is given by (% yield × given moles of limiting reagent).

Train Your Brain

Example 29: $\underset{10\text{mole}}{A} + \underset{10\text{mole}}{5B} \longrightarrow C + 3D$, in this reaction which is a L.R.?

Sol. For A For B

$\frac{10}{1} = 10$ $\frac{10}{5} = 2$

2 < 10 So, B is L.R.

Example 30: $\underset{4g}{H_2(g)} + \underset{32g}{\frac{1}{2}O_2(g)} \longrightarrow H_2O(g)$; in the above reaction, what is the volume of water vapour produced at STP?
(*a*) 4.48 L (*b*) 44.8 L
(*c*) 2.24 L (*d*) 11.2 L

Sol. (*b*) $\underset{4g}{H_2(g)} + \underset{32g}{\frac{1}{2}O_2(g)} \longrightarrow H_2O(g)$

For H_2 For O_2

$n = \frac{4}{2} = 2\text{mol}$ $n = \frac{32}{32} = 1\text{mol}$

For L.R. $\frac{2}{1} = 2$ $\frac{1}{\frac{1}{2}} = 2$ mol

Moles of $H_2O_{(g)}$ produced $= 2 \text{ mol} = \frac{V}{22.4}$

Both H_2 & O_2 are L.R.

Volume of $H_2O_{(g)}$ produced at STP = 22.4 × 2

= 44.8 litre

Example 31: At STP, In a container 100 mL N_2 and 100 mL of H_2 are mixed together. Then find out the produced volume of NH_3.
(*a*) 6.66 mL (*b*) 66.6 mL
(*c*) 3.33 mL (*d*) 5.55 mL

Sol. (*b*) Balanced equation will be $N_2 + 3H_2 \rightarrow 2NH_3$.

Given 100mL 100mL

For determination of Limiting reagent. Divide the given quantities by stoichiometry coefficients

$\frac{100}{1} = 100$ $\frac{100}{3} = 33.3$ (Limiting reagent)

In this reaction H_2 is limiting reagent so reaction will proceed according to H_2.

According to stoichiometry from 3 mL of H_2 produced volume of $NH_3 = 2$ ml

That is from 100 ml of H_2 produced volume of

$$NH_3 = \frac{2}{3} \times 100 = 66.6 \text{ mL}$$

Example 32: Number of moles of NH_3 produced if 140 gm of N_2 reacts with 40 gm of di-hydrogen. (Given % yield of reaction is 50%)

(*a*) 12 (*b*) 10 (*c*) 5 (*d*) 6

Sol. (*c*) $N_2 + 3H_2 \xrightarrow{50\%} 2NH_3$

140 gm 40 gm

or 5 mol 20 mol

$\therefore$ Number of moles of NH_3 produced = 5×2×0.5 = 5 mole

Concept Application

29. 4 mole of $MgCO_3$ is reacted with 6 moles of HCl solution. Find the volume of CO_2 gas (in litres) produced at STP, the reaction is:

$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$.

(*a*) 11.2 (*b*) 22.4

(*c*) 67.2 (*d*) 44.8

30. For a reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; which of the following reaction mixtures has dihydrogen (H_2) as a limiting reagent, :

(*a*) 14g of N_2 + 4g of H_2 (*b*) 35g of N_2 + 8g of H_2

(*c*) 28g of N_2 + 6g of H_2 (*d*) 56g of N_2 + 10g of H_2

31. The percent yield for the following reaction carried out in carbon tetrachloride (CCl_4) solution is 80%.

$Br_2 + Cl_2 \longrightarrow 2BrCl$

How many moles of BrCl is formed from the reaction of 0.025 mol Br_2 and 0.025 mol Cl_2?

(*a*) 0.04 (*b*) 0.08]

(*c*) 0.02 (*d*) 0.01

32. If 240 g of carbon is taken in a container to convert it completely to CO_2 but in industry it has been found that 280 g of CO was also formed along with CO_2. Find the mole percentage yield of CO_2. The reactions occurring are:

$$C + O_2 \longrightarrow CO_2; C + \frac{1}{2}O_2 \longrightarrow CO$$

(*a*) 25 (*b*) 50 (*c*) 75 (*d*) 35

ADVANCED LEARNING

SEQUENTIAL REACTION

Here, we solve problems in which the products of one reaction are used up in one or more subsequent reactions. In order to attempt such problems the following solving strategy has to be used.

(*i*) The balanced and molecular equations are written for all reactions involved separately.

(*ii*) Later the equations are multiplied, as a whole, by suitable factors, so that products of one reaction which are utilized in subsequent reactions are cancelled out.

(*iii*) The final reaction obtained is used to find out the required quantities.

Illustration: How many kilograms of pure H_2SO_4 could be obtained from one kilogram of pure iron pyrites (FeS_2) according to the following reactions?

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
$$2SO_2 + O_2 \longrightarrow 2SO_3$$
$$SO_2 + H_2O \longrightarrow H_2SO_4$$

(*a*) 0.184kg (*b*) 1.633kg

(*c*) 2.643kg (*d*) 3.234kg

Sol. Gram molecular weight of FeS_2 = 120g

Gram molecular weight of H_2SO_4 = 98 g

Let us multiply the equations with suitable factors.

$$4FeS_2 + 11\,O_2 \longrightarrow 2Fe_2O_3 + 8\,SO_2$$
$$2SO_2 + O_2 \longrightarrow 2SO_3 \times 4$$
$$SO_3 + H_2O \longrightarrow H_2SO_4 \times 8$$

$$\left\{\begin{array}{l} 4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + \cancel{8SO_2} \\ \cancel{8SO_2} + 4O_2 \longrightarrow \cancel{8SO_3} \\ \cancel{8SO_3} + 8H_2O \longrightarrow 8H_2SO_4 \end{array}\right.$$

$$\overline{4FeS_2 + 15O_2 + 8H_2O \longrightarrow 2Fe_2O_3 + 8H_2SO_4}$$

From the above, it is clear that, 4 moles of FeS_2 produces 8 moles of H_2SO_4 (or)

1 mole of $FeS_2 \xrightarrow{\text{produces}}$ 2 moles of H_2SO_4

$\therefore$ 120g (1 mole) of $FeS_2 \xrightarrow{\text{produces}}$ 2 × 98 g (2 moles) of H_2SO_4

$$\therefore 1000\text{g (1 kg) of } FeS_2 \xrightarrow{\text{produces}} \frac{1000 \times 2 \times 98}{120} = 1633.33 \text{ g}$$

or 1.633 kg of H_2SO_4

Therefore, 1.633 kg of H_2SO_4 is produced from 1 kg of iron pyrites.

Illustration: 20 g of $KClO_3$ on heating give enough oxygen to react completely with hydrogen produced by the action of dil. H_2SO_4 on zinc. Find the weight of zinc required for the purpose. The reactions are as follows: (K = 39, Zn = 65, Cl = 35.5) (*i*) $2KClO_3 \longrightarrow 2KCl + 3O_2$

(*ii*) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

(*iii*) $H_2 + O_2 \longrightarrow H_2O$

(*a*) 13.84g (*b*) 21.48g

(*c*) 31.84g (*d*) 43.48g

Sol. Gram molecular weight of $KClO_3 = 122.5$ g

Gram atomic weight of zinc = 65 g

Let us multiply the equations with suitable factors.

$$\left.\begin{array}{l} 2KClO_3 \longrightarrow 2KCl + 3O_2 \\ Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \times 6 \\ H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \times 6 \end{array}\right\}$$

$$2KClO_3 \longrightarrow 2KCl + \cancel{3O_2}$$

$$6Zn + 6H_2SO_4 \longrightarrow 6ZnSO_4 + \cancel{6H_2}$$

$$\cancel{6H_2} + \cancel{3O_2} \longrightarrow 6H_2O$$

$$2KClO_3 + 6Zn + 6H_2SO_4 \longrightarrow 2KCl + 6ZnSO_4 + 6H_2O$$

From the above, it is clear that, 2 moles of $KClO_3$ requires 6 moles of Zn (or)

1 mole of $KClO_3 \xrightarrow{\text{requires}}$ 3 moles of Zn

$\therefore$ 122.5 g (1 mole) of $KClO_3 \xrightarrow{\text{requires}} 3 \times 65$ g (3 moles) of Zn

$\therefore$ 20 g of $KClO_3 \xrightarrow{\text{requires}} \frac{20 \times 3 \times 65}{122.5} = 31.84$ g of Zn

Therefore, 31.84 g of Zn is required for the given purpose.

POAC

POAC is based upon law of conservation of mass. Atoms are conserved, hence moles of atoms shall also be conserved in a chemical reaction (but not in nuclear reactions.)

Consider the reaction:

$KClO_3(s) \rightarrow KCl(s) + O_2(g)$ (unbalanced chemical reaction)

Apply POAC for K atoms.

Moles of K atoms in reactant ($KClO_3$) = moles of K atoms in product (KCl)

Moles of K atoms in $KClO_3$ = 1 × moles of $KClO_3$

and moles of K atoms in KCl = 1 × moles of KCl.

$\therefore$ moles of $KClO_3$ = moles of KCl

$$\text{or } \frac{\text{wt. of } KClO_3 \text{ in g}}{\text{mol. wt. of } KClO_3} = \frac{\text{wt. of KCl in g}}{\text{mol. wt. of KCl}}$$

Again, applying the POAC for O atoms,

moles of O in $KClO_3$ = 3 × moles of $KClO_3$

moles of O in O_2 = 2 × moles of O_2

$\therefore$ 3 × moles of $KClO_3$ = 2 × moles of O_2

$$\text{or } 3 \times \frac{\text{wt. of } KClO_3}{\text{mol. wt. of } KClO_3} = 2 \times \frac{\text{vol. of } O_2 \text{ at STP}}{22.4 \text{ L}}$$

Illustration: 0.32 mole of $LiAlH_4$ in ether solution was placed in a flask and 74 g (1 moles) of t-butyl alcohol was added. The product is $LiAlHC_{12}H_{27}O_3$. Find the weight of the product if lithium atoms are conserved.

[Li = 7, Al = 27, H = 1, C = 12, O = 16]

Sol. Applying POAC for lithium atoms,

1 × moles of $LiAlH_4$ = 1 × moles of LiAlH $C_{12}H_{27}O_3$

$$0.32 = 1 \times \frac{\text{weight of LiAlH } C_{12}H_{27}O_3}{254}$$

wt. of LiAlH $C_{12}H_{27}O_3$ = 81.28 g.

Illustration: 27.6 g K_2CO_3 was treated by a series of reagents so as to convert all of its carbon to $K_2Zn_3[Fe(CN)_6]_2$. Calculate the weight of the product.

[mol. wt. of K_2CO_3 = 138 and mol. wt. of $K_2Zn_3[Fe(CN)_6]_2$ = 698]

Sol. Here we have not knowledge about series of chemical reactions but we known about initial reactant and final product accordingly

$$K_2CO_3 \xrightarrow[\text{Steps}]{\text{Several}} K_2Zn_3[Fe(CN)_6]_2$$

Since C atoms are conserved, applying POAC for C atoms,

moles of C in K_2CO_3 = moles of C in $K_2Zn_3[Fe(CN)_6]_2$

1 × moles of K_2CO_3 = 12 × moles of $K_2Zn_3[Fe(CN)_6]_2$

$$\frac{\text{wt. of } K_2CO_3}{\text{mol. wt. of } K_2CO_3} = 12 \times \frac{\text{wt. of the product}}{\text{mol. wt. of product}}$$

$$\text{wt. of } K_2Zn_3[Fe(CN)_6]_2 = \frac{27.6}{138} \times \frac{698}{12} = 11.6 \text{ g}$$

STRENGTH (LABELLING) OF OLEUM

Oleum is SO_3 dissolved in 100% H_2SO_4. Sometimes, oleum is reported as more than 100% by weight, say y% (where y > 100). This means that (y - 100) grams of water, when added to 100 g of given oleum sample, will combine with all the free SO_3 in the oleum to give 100% sulphuric acid. Hence,

weight % of free SO_3 in oleum = 80 (y–100)/18.

Example: If in a sample of oleum, mole fraction of SO_3 is 0.5. Label the oleum sample.

Sol. Total moles = 1

Moles of SO_3 = mole of H_2SO_4 = 0.5

Total Mass of SO_3 & H_2SO_4 = 40 + 49 = 89 gm

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

0.5 0.5

Mass of H_2O required = 0.5 × 18 = 9 gm

89 gm require 9 gm H_2O

$$100 \text{ gm require} = \frac{9}{89} \times 100 = 10.11 \text{ gm}$$

% Labelling = (100 + 10.11) = 110.11%

Aarambh (Solved Examples)

1. 1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. The law shown by above data is:
   (*a*) Law of constant proportion
   (*b*) Law of multiple proportion
   (*c*) Law of reciprocal proportion
   (*d*) All of the above

Sol. In the first sample of oxide,

Weight of metal = 1.80 g;

Weight of oxygen = (3.0 – 1.80) g = 1.2 g

$$\therefore \frac{\text{wt of metal}}{\text{wt of oxygen}} = \frac{1.80\text{g}}{1.2\text{g}} = 1.5$$

In the second sample of the oxide,

Weight of metal = 1.50 g;

Weight of oxygen = (2.50 – 1.50) g = 1 g

$$\frac{\text{wt of metal}}{\text{wt of oxygen}} = 1.5$$

Thus, in both samples of the oxide, the proportions of the weights of the metal and oxygen are fixed. Hence the results follow the law of constant proportion.

Therefore, option (*a*) is the correct answer.

2. Calculate the total charge present on 4.2 gm of N^{3-}.

(*a*) 8.67×10^4 C	(*b*) 9.05×10^4 C
(*c*) 8.67×10^3 C	(*d*) 7.67×10^4 C

Sol. $\text{Mole} = \frac{\text{wt.in gm}}{\text{Ionic wt.}} = \frac{4.2}{14} = 0.3$

Total no. of ions = $0.3 \times N_A$ ions.

Total charge = $0.3\ N_A \times 3 \times 1.6 \times 10^{-19}$ C

$= 0.3 \times 6.022 \times 10^{23} \times 3 \times 1.6 \times 10^{-19} = 8.67 \times 10^4$ C

Therefore, option (*a*) is the correct answer.

3. How many carbon atoms are present in 0.35 mol of $C_6H_{12}O_6$?
   (*a*) 6.022×10^{23} carbon atoms.
   (*b*) 1.26×10^{23} carbon atoms.
   (*c*) 1.26×10^{24} carbon atoms.
   (*d*) 6.022×10^{24} carbon atoms.

Sol. $\because$ 1 mol of $C_6H_{12}O_6$ has 6 N_A atoms of C

$\therefore$ 0.35 mol of $C_6H_{12}O_6$ has $6 \times 0.35\ N_A$ atoms of C

$= 2.1\ N_A$ atoms $= 2.1 \times 6.022 \times 10^{23} = 1.26 \times 10^{24}$ carbon atoms.

Therefore, option (*c*) is the correct answer.

4. How many molecules are present in 5.23 gm of glucose ($C_6H_{12}O_6$)?

(*a*) 1.65×10^{22}	(*b*) 1.75×10^{22}
(*c*) 1.75×10^{21}	(*d*) None of these

Sol. $\because$ 180 gm glucose has = N_A molecules

$$\therefore \text{5.23 gm glucose has} = \frac{5.23 \times 6.022 \times 10^{23}}{180}$$

$= 1.75 \times 10^{22}$ molecules

Therefore, option (*b*) is the correct answer.

5. A sample of (C_2H_6) ethane has the same mass as 10^7 molecules of methane. How many C_2H_6 molecules does the sample contain?

(*a*) 5.34×10^6	(*b*) 1.26×10^8
(*c*) 4.26×10^6	(*d*) 6.022×10^6

Sol. Moles of $CH_4 = \frac{10^7}{N_A}$

Mass of $CH_4 = \frac{10^7}{N_A} \times 16$ = mass of C_2H_6

So Moles of $C_2H_6 = \frac{10^7 \times 16}{N_A \times 30}$

So no. of molecules of $C_2H_6 = \frac{10^7 \times 16}{N_A \times 30} \times N_A = 5.34 \times 10^6$.

Therefore, option (*a*) is the correct answer.

6. From 160 g of SO_2 (g) sample, 1.2046×10^{24} molecules of SO_2 are removed then find out the volume of left over SO_2 (g) at STP.

(*a*) 11.2 L	(*b*) 12.5 L
(*c*) 9.5 L	(*d*) 10.8 L

Sol. Given moles $= \frac{160}{64} = 2.5$.

Removed moles $= \frac{1.2046 \times 10^{24}}{6.022 \times 10^{23}} = 2$.

So left moles = 0.5.

Volume left at STP = 0.5 × 22.4 = 11.2 L.

Therefore, option (*a*) is the correct answer.

7. 14 g of Nitrogen gas and 22 g of CO_2 gas are mixed together. Find the volume of gaseous mixture at STP.

(*a*) 10.2 L	(*b*) 12.2 L
(*c*) 15.5 L	(*d*) 22.4 L

Sol. Moles of $N_2 = \frac{14}{28} = 0.5$.

Moles of $CO_2 = \frac{22}{44} = 0.5$.

So total moles = 0.5 + 0.5 = 1.

So vol. at STP = 1 × 22.4 = 22.4 L.

Therefore, option (*d*) is the correct answer.

8. How many years it would take to spend Avogadro's number of rupees at the rate of 1 million rupees per second?

(*a*) 19.098×10^{19} years	(*b*) 19.098 years
(*c*) 19.098×10^9 years	(*d*) None of these

Sol. ∵ 10^6 rupees are spent in 1 sec.

∴ 6.022×10^{23} rupees are spent in

$$\frac{1\times6.022\times10^{23}}{10^6}\ \text{sec}$$

or $\dfrac{1\times6.022\times10^{23}}{10^6\times60\times60\times24\times365}$ years = 19.098×10^9 years

Therefore, option (*c*) is the correct answer.

9. The density of O_2 at STP is 1.429g/litre. Calculate the standard molar volume of gas.

(*a*) 22.4 lit. (*b*) 11.2 lit (*c*) 33.6 lit (*d*) 5,6 lit.

Sol. ∵ 1.429 gm of O_2 gas occupies volume = 1 litre.

∴ 32 gm of O_2 gas occupies = $\dfrac{32}{1.429}$ = 22.4 litre/mol.

Therefore, option (*a*) is the correct answer.

10. Calculate the weight of lime (CaO) obtained by heating 200 kg of 95% pure lime stone ($CaCO_3$).

(*a*) 104.4 kg (*b*) 105.4 kg

(*c*) 212.8 kg (*d*) 106.4 kg

Sol. ∵ 100 kg impure sample has pure

$CaCO_3$ = 95 kg

∴ 200 kg impure sample has pure $CaCO_3$

$= \dfrac{95\times200}{100} = 190$ kg.

$CaCO_3 \rightarrow CaO + CO_2$

∵ 100 kg $CaCO_3$ gives CaO = 56 kg.

∴ 190 kg $CaCO_3$ gives CaO = $\dfrac{56\times190}{100}$ = 106.4 kg.

Therefore, option (*d*) is the correct answer.

11. A compound containing beryllium has the following composition, Be = 6.1%, N = 37.8%, Cl=48%, H = 8.1%. One mole of the compound has mass of 148g and average atomic mass of beryllium is 9. The molecular formula of the compound is:

(*a*) $BeN_4H_{12}Cl_2$ (*b*) $BeN_2H_{10}Cl$

(*c*) $BeN_4H_2Cl_3$ (*d*) $Be_2N_4H_{10}Cl_2$

Sol.

Element	%	%/A	Simplest ratio
Be	6.1	6.1/9 = 0.677	1
N	37.8	37.8/14 = 2.7	4
Cl	48	48/35.5 = 1.35	2
H	8.1	8.1/1 = 8.1	12

Empirical formula = $BeN_4Cl_2H_{12}$

= 9 + 56 + 71 + 12

= 148 ⇒ n = 1

Molecular formula = $BeN_4Cl_2H_{12}$

Therefore, option (*a*) is the correct answer.

12. One litre of a mixture of CO and CO_2 is passed through red hot charcoal in tube. The new volume becomes 1.4 litre. Find out % composition of mixture by volume. All measurements are made at same P and T.

(*a*) CO_2 40%, CO 60% (*b*) CO_2 60%, CO 40%

(*c*) CO_2 25%, CO 75% (*d*) CO_2 30%, CO 70%

Sol. On passing through charcoal only CO_2 reduces to CO.

$CO + C \longrightarrow$ No reaction

Volume a

$CO_2 + C \longrightarrow 2\,CO$

Volume before reaction b 0

Volume after reaction 0 2b

As given a + b = 1 and a + 2b = 1.4

∴ b = 0.4 litre ∴ % of b = $\dfrac{0.4}{1}$ × 100 = 40 %

∴ a = 0.6 litre ∴ % of a = $\dfrac{0.6}{1}$ × 100 = 60 %

Therefore, option (*a*) is the correct answer.

13. Calculate the molarity of H^+ ion in the resulting solution when 200 ml 0.5M HCl is mixed with 200 ml 0.5M H_2SO_4

Sol. n_{H^+} = 0.1 (from HCl) & n_{H^+} = 0.2 (from H_2SO_4)

Total H^+ = n_{H^+} (from HCl) + n_{H^+} (from H_2SO_4) = 0.1 + 0.2 = 0.3

Total volume = 200 + 200 = 400 mL = 0.4 L

MR = Resultant molarity = $\dfrac{n_{H^+}}{V_{\text{solution}}} = \dfrac{0.3}{0.4}$ = 0.75 M Ans.

Therefore, [0.75] is the correct answer.

14. What are the final concentration of all the ions when following are mixed 50 ml of 0.12 M $Fe(NO_3)_3$ + 100 ml of 0.1 M $FeCl_3$ + 100 ml of 0.26 M $Mg(NO_3)_2$.

Sol. $[NO_3^-] = \dfrac{50\times0.12\times3+100\times0.26\times2}{250} = \dfrac{18+52}{250} = \dfrac{70}{250} = 0.28$

$[Cl^-]$ = 0.12 M; $[Mg^{++}]$ = 0.104 M; $[Fe^{3+}]$ = 0.064 M

Therefore, [0.064] is the correct answer.

15. A sample of 3 g containing Na_2CO_3 and $NaHCO_3$ loses 0.248 g when heated to 300°C, the temperature at which $NaHCO_3$ decomposes to Na_2CO_3, CO_2 and H_2O. What is the percentage of Na_2CO_3 in the given mixture?

Sol. The loss in weight is due to removal of CO_2 and H_2O which escape out on heating.

wt. of Na_2CO_3 in the product = 3.00 – 0.248 = 2.752 g

Let wt. of Na_2CO_3 in the mixture be x g

∴ wt. of $NaHCO_3$ = (3.00 – x) g

Since Na_2CO_3 in the products contains x g of unchanged reactant Na_2CO_3 and rest produced from $NaHCO_3$.

The wt. of Na_2CO_3 produced by $NaHCO_3$ = (2.752 – x)g

$NaHCO_3 \longrightarrow Na_2CO_3 + (H_2O + CO_2)\uparrow$

(3.0 – x) (2.752 – x)

Applying POAC for Na atom

1 × moles of $NaHCO_3$ = 2 × moles of Na_2CO_3

$\Rightarrow \dfrac{(3-x)}{84} = 2\times\dfrac{(2.752-x)}{106}$

∴ x = 2.328 g

∴ % of Na_2CO_3 = $\dfrac{2.328}{3}$ × 100 = 77.6 %

Therefore, [77.6] is the correct answer.

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of the solution is
   (*a*) 0.02 M (*b*) 0.01 M
   (*c*) 0.001 M (*d*) 0.1 M

2. 10 mol of Zn react with 10 mol of HCl. Calculate the number of moles of H_2 produced.
   (*a*) 5 mol (*b*) 10 mol
   (*c*) 20 mol (*d*) 2.5 mol

3. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02M H_2SO_4 Solution is
   (*a*) 12.044×10^{20} molecules
   (*b*) 6.022×10^{23} molecules
   (*c*) 1×10^{23} molecules
   (*d*) 12.044×10^{23} molecules

4. What is the mass percent of carbon in carbon dioxide?
   (*a*) 0.034% (*b*) 27.27%
   (*c*) 3.4% (*d*) 28.7%

5. Which of the following statements about a compound is incorrect?
   (*a*) A molecule of a compound has atoms of different elements.
   (*b*) A compound cannot be separated into its constituent elements by physical methods of separation.
   (*c*) A compound retains the physical properties of its constituent elements.
   (*d*) The ratio of atoms of different elements in a compound is fixed.

6. Which of the following statements is correct about the reaction given below:
$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(g)$$
   (*a*) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product therefore it follows law of conservation of mass.
   (*b*) Total mass of reactants = total mass of product; therefore, law of multiple proportions is followed.
   (*c*) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess.
   (*d*) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess.

7. Number of atoms of He in 100 u of He (Atomic mass of He is 4 u)
   (*a*) 25 (*b*) 50
   (*c*) 100 (*d*) 400

8. A gaseous hydrocarbons gives upon combustion, 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is:
   (*a*) C_6H_5 (*b*) C_7H_8
   (*c*) C_2H_4 (*d*) C_3H_4

9. **Assertion:** No. of moles of H_2 in 0.224 L of hydrogen is 0.01 mole.
   Reason: 22.4 L of H_2 at STP contain 6.022×10^{23} moles.
   (*a*) Both Assertion and Reason are true and Reason is correct explanation of Assertion.
   (*b*) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.
   (*c*) Assertion is true but Reason is false.
   (*d*) Assertion is false but Reason is true.

10. **Assertion:** The empirical mass of ethene is half of its molecular mass.
   Reason: The empirical formula represents the whole number ratio of various atoms present in a compound.
   (*a*) Both Assertion and Reason are true and Reason is correct explanation of Assertion.
   (*b*) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.
   (*c*) Assertion is true but Reason is false.
   (*d*) Assertion is false but Reason is true.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the following:

	List-I		List-II
(i)	Molarity	p.	For very dilute solution
(ii)	Molality	q.	No units
(iii)	mole fraction	r.	Mol L^{-1}
(iv)	ppm	s.	independent of temperature

12. Match the following:

	List-I		List-II
(i)	88 g of CO_2	p.	0.25 mol
(ii)	6.022×10^{23} molecules of H_2O	q.	2 mol
(iii)	5.6 litres of O_2 at STP	r.	1 mol
(iv)	96 g of O_2	s.	6.022×10^{23} molecules
(v)	1 mol of any gas	t	3 mol

SHORT ANSWER TYPE QUESTIONS

13. Volume of a solution changes with change in temperature, then, will be molality of the solution be affected by temperature? Give reason for your answer.

14. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of each component in the solution. Also, determine the molarity of solution (specific gravity of solution is $1 g mL^{-1}$).

15. A solution is prepared by adding 2g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

16. How many atoms and molecules are present in 124 gm of phosphorus (P_4).

17. The cost of table salt (NaCl) is Rs. 10 per Kg. Calculate its cost per mole. (Molar mass of NaCl is 58.5 g mol^{-1})

18. Calculate the mole fraction of the solute in a 1.00 molal aqueous solution.

LONG ANSWER TYPE QUESTIONS

19. A vessel contains 1.6 g of dioxygen at STP (273.15 K, 1 atm pressure). The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. Calculate

(*a*) volume of the new vessel.

(*b*) number of molecules of dioxygen.

20. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction given below:

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

What mass of $CaCl_2$ will be formed when 250 mL of 0.76 M HCl reacts with 1000 g of $CaCO_3$? Name the limiting reagent. Calculate the number of moles of $CaCl_2$ formed in the reaction.

21. In a compound $C_xH_yO_z$, the mass % of C and H is 6 : 1 and the amount of oxygen present is equal to the half of the oxygen required to react completely C_xH_y. Find the empirical formula of the compound.

22. An LPG cylinder weighs 14.8 Kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of cylinder is reduced to 23.2 Kg. Find the volume of n-butane in cubic meters used up at 27°C and 1 atm (Molecular weight of n-butane = 58).

23. A box contains some identical red coloured balls, labelled as A, each weighing 2 grams. Another box contains identical bule coloured balls, labelled as B, each weighing 5 grams. Consider the combinations AB, AB_2, A_2B and A_2B_3 and show that law of multiple.

CASE STUDY BASED QUESTIONS

24. The ideas underlying our modern understanding of thermodynamics and kinetic theory were developed during the nineteenth century. Central to these developments was the discovery that matter reacting chemically does not do so simply between equal masses of the samples involved. We now call the study of this phenomenon 'stoichiometry', defined as: 'the relationship between the amounts of substance that react together, and the products that are formed'.

Another development during the nineteenth century that was central to our modern understanding of the chemical nature of matter was the observation by Avogadro that 'equal volumes of ideal or perfect gases, at the same temperature and pressure, contain the same number of particles, or molecules'. This is now known as Avogadro's law. It provides the motivation to formulate expressions for the quantity of a sample that reacts with another sample. The most notable example of such a formulation is the gram-molecule, which has been used to refer to both a unit and a quantity.

The following questions are multiple choice questions. Choose the most appropriate answer:

I. The concept of stoichiometry mentioned in the study is based on the

(*a*) formation of chemical bonds.

(*b*) amount of reactant and product involved in a chemical reaction.

(*c*) idea of temperature and pressure required for the reaction to occur.

(*d*) oxidation states of reactant and product involved.

II. How much gram-molecules of H_2O are produced on combustion of 32 g of methane in excess oxygen?

(*a*) 72 (*b*) 4 (*c*) 2 (*d*) 36

III. When an antacid tablet is used, $Ca(OH)_2$ reacts with HCl in the stomach to form inert $CaCl_2$ and H_2O. If the molar mass of $Ca(OH)_2$ is 75 g/mol, how many moles of HCl are required to fully react with 150 g of $Ca(OH)_2$?

(*a*) 4 (*b*) 1 (*c*) 8 (*d*) 2

IV. What must be held constant when applying Avogadro's law?

(*a*) pressure and temperature

(*b*) volume and temperature

(*c*) moles and temperature

(*d*) pressure and volume

Prarambh (Topicwise)

FUNDAMENTAL QUANTITIES, LAWS OF CHEMICAL COMBINATION

1. Express the result of (0.582 + 324.65) to the appropriate number of significant figures:
(*a*) 325.24 (*b*) 325.23
(*c*) 325.2 (*d*) 325.232

2. The correctly reported answer of the area of rectangle which is 12.34 cm long and 1.23 cm wide is :
(*a*) 15.2 m^2 (*b*) 15.2 cm^2
(c) 15.1 cm^2 (*d*) 15.17 cm^2

3. If an object has a mass of 0.2876 g, then find the mass of nine such objects:
(*a*) 2.5884 g (*b*) 2.5886 g (*c*) 2.588 g (*d*) 2.5 g

4. Two elements X and Y combine in gaseous state to form XY in the ratio 1:35.5 by mass. The mass of Y that will be required to react with 2 g of X is:
(*a*) 7.1 g (*b*) 3.55 g (*c*) 71 g (*d*) 35.5 g

5. 4.4 g of an oxide of nitrogen gives 2.24 L of nitrogen and 60 g of another oxide of nitrogen gives 22.4 L of nitrogen at S.T.P. The data illustrates:
(*a*) Law of conservation of mass
(*b*) Law of constant proportions
(*c*) Law of multiple proportions
(*d*) Law of reciprocal proportions

6. Two elements X and Y combine to form compounds A, B and C. The ratio of different masses of Y which combine with a fixed mass of X in A, B and C is 1 : 3 : 5. If 32 parts by mass of X combines with 84 parts by mass of Y in B, then in C, 16 parts by mass of X will combine with:
(*a*) 14 parts by mass of Y (*b*) 42 parts by mass of Y
(c) 70 parts by mass of Y (*d*) 84 parts by mass of Y

ATOMIC MASS & MOLECULAR MASS, MOLE CONCEPT AND APPLICATIONS

7. 1 amu is equal to:
(*a*) $\frac{1}{12}$ of mass of C^{12} atom
(*b*) $\frac{1}{14}$ of mass of O^{16} atom
(*c*) 1 g of H_2
(*d*) 1.66×10^{-23} kg

8. 1 mol of CH_4 contains:
(*a*) 6.02×10^{23} atoms of H
(*b*) 4 g-atom of Hydrogen
(*c*) 1.81×10^{23} molecules of CH_4
(*d*) 3.0 g of carbon

9. 7.5 grams of a gas occupy 5.6 litres of volume at STP, the gas is:
(*a*) NO (*b*) N_2O (*c*) CO (*d*) CO_2

10. The number of atoms in 4.25 g of NH_3 is approximately:
(*a*) 1×10^{23} (*b*) 2×10^{23} (*c*) 4×10^{23} (*d*) 6×10^{23}

11. One litre of a gas at STP weighs 1.16 g. The possible gas is:
(*a*) C_2H_2 (*b*) CO
(*c*) O_2 (*d*) CH_4

12. The mass of a molecule of water is approximately:
(*a*) 3×10^{-26} kg (*b*) 3×10^{-25} kg
(*c*) 1.5×10^{-26} kg (*d*) 2.5×10^{-26} kg

13. If N_A is Avogadro's number, then number of valence electrons in 4.2 g of nitride ions (N^{3-}) is:
(*a*) 2.4 N_A (*b*) 4.2 N_A
(*c*) 1.6 N_A (*d*) 3.2 N_A

14. The number of molecules at STP in 1 ml of an ideal gas will be:
(*a*) 6×10^{23} (*b*) 2.69×10^{19}
(*c*) 2.69×10^{23} (*d*) None of these

15. Volume of a gas at STP is 1.12×10^{-7} cc. The number of molecules in it are:
(*a*) 3.01×10^{20} (*b*) 3.01×10^{12}
(*c*) 3.01×10^{23} (*d*) 3.01×10^{24}

16. 4.4 g of an unknown gas occupies 2.24 L of volume at standard temperature and pressure. The gas may be
(*a*) Carbon dioxide (*b*) Carbon monoxide
(*c*) Oxygen (*d*) Sulphur dioxide

17. The number of oxygen atoms in 4.4 g of CO_2 is approx.
(*a*) 1.2×10^{23} (*b*) 6×10^{22}
(*c*) 6×10^{23} (*d*) 12×10^{23}

18. The total number of protons in 10 g of calcium carbonate is ($N_A = 6.022 \times 10^{23}$)
(*a*) 1.5057×10^{24} (*b*) 2.0478×10^{24}
(*c*) 3.0115×10^{24} (*d*) 4.0956×10^{24}

19. Number of molecules in 100 ml each of O_2, NH_3 and CO_2 at STP are
(*a*) In the order $CO_2 > O_2 > NH_3$
(*b*) In the order $NH_3 > O_2 > CO_2$
(*c*) The same in all
(*d*) In the order $NH_3 > CO_2 > O_2$

20. The number of water molecules in 1 litre of water is
(*a*) 18 (*b*) 18×1000
(*c*) N_A (*d*) 55.55 N_A

21. 2 g of oxygen contains number of atoms equal to that in
(*a*) 0.5 g of hydrogen (*b*) 4 g of sulphur
(*c*) 7 g of nitrogen (*d*) 2.3 g of sodium

PERCENTAGE COMPOSITION, EMPIRICAL FORMULA & MOLECULAR FORMULA

22. Caffeine has a molecular weight of 194. If it contains 28.9% by mass of nitrogen, number of atoms of nitrogen in one molecule of caffeine is:
(*a*) 4 (*b*) 6 (*c*) 2 (*d*) 3

23. The percentage of oxygen in NaOH is:
(*a*) 40 (*b*) 60 (*c*) 8 (*d*) 10

24. A compound (60 g) on analysis gave C = 24 g, H = 4 g, O = 32 g. Its empirical formula is:
(*a*) $C_2H_2O_2$ (*b*) C_2H_2O (*c*) CH_2O_2 (*d*) CH_2O

25. What is the % of H_2O in $Fe(CNS)_3 \cdot 3H_2O$?
(*a*) 45 (*b*) 30 (*c*) 19 (*d*) 25

26. A hydrocarbon contains 86% carbon. Then, the hydrocarbon is an:
(*a*) Alkane (*b*) Alkene (*c*) Alkyne (*d*) Arene

27. The simplest formula of a compound containing 50% of element X (atomic mass 10) and 50% of element *Y* (atomic mass 20) is:
(*a*) XY (*b*) X_2Y (*c*) XY_3 (*d*) X_2Y_3

28. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67,200. The number of iron atoms (At. wt. of Fe = 56) present in one molecule of haemoglobin is:
(*a*) 6 (*b*) 1 (*c*) 4 (*d*) 2

CONCENTRATION TERMS

29. What is the molarity of NaOH solution if 250 mL of it contains 1 mg of NaOH?
(*a*) 10^{-1} M (*b*) 10^{-2} M (*c*) 10^{-4} M (*d*) 10^{-3} M

30. Molarity of H_2SO_4 (density 1.8 g/mL) is 18 M. The molality of this H_2SO_4 is
(*a*) 36 (*b*) 200 (*c*) 500 (*d*) 18

31. The percentage of sodium in a breakfast cereal be labeled as 110 mg of sodium per 100 g of cereal is
(*a*) 11% (*b*) 1.10% (*c*) 0.11% (*d*) 1.10%

32. 200 ml 3M NaOH is mixed with 300 ml 2 M NaOH forming a solution of density 1200 kg m^{-3}. Then molality of final solution is
(*a*) 2.2 m (*b*) 3 m (*c*) 2.4 m (*d*) 2 m

33. Calculate molality of 0.2 M urea solution having density 1.2 gm/ml
(*a*) $\approx \frac{1}{6}$ m (*b*) $\approx \frac{1}{3}$ m (*c*) $\approx \frac{1}{9}$ m (*d*) $\approx \frac{1}{12}$ m

34. Commercial HNO_3(aq) has density 1.41 g/ml and is 10M. Then mass percentage of solution is
(*a*) $\frac{100}{3}$% (*b*) 50% (*c*) 75% (*d*) 25%

35. 0.02 gm of an unknown substance is dissolved in 3.9 gm of benzene. The molality of solution is 0.08 m. Calculate the molecular mass of unknown substance.

(*a*) 60 g/mol (*b*) 164 g/mol
(*c*) 264 g/mol (*d*) 64.1 g/mol

36. A 500 g solution has 0.1 g fluoride concentration. Then fluoride concentration in term of ppm will be:
(*a*) 200 ppm (*b*) 100 ppm
(*c*) 400 ppm (*d*) 50 ppm

STOICHIOMETRY, EQUATION BASED CALCULATIONS

37. In the reaction;
$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$, when 1 mole of ammonia and 1 mole of O_2 are made to react to completion:
(*a*) 1.0 mole of H_2O is produced.
(*b*) 1.0 mole of NO will be produced.
(*c*) All the oxygen will be consumed.
(*d*) All the ammonia will be consumed.

38. H_2 evolved at STP on complete reaction of 27 g of aluminium with excess of aqueous NaOH would be:

$$Al + H_2O + NaOH \rightarrow NaAlO_2 + \frac{3}{2}H_2$$

(*a*) 22.4 litres (*b*) 44.8 litres
(*c*) 67.2 litres (*d*) 33.6 litres

39. 12 g of Mg (at. mass 24) will react completely with acid to give:
(*a*) One mole of H_2
(*b*) 1/2 mole of H_2
(*c*) 2/3 mole of O_2
(*d*) Both 1/2 mol of H_2 and 1/2 mol of O_2

40. 100 g $CaCO_3$ reacts with 1 litre 1 N HCl. On completion of reaction, how much weight of CO_2 will be obtained?
(*a*) 5.5 g (*b*) 11 g (*c*) 22 g (*d*) 33 g

41. What weight of HNO_3 is needed to convert 5 g of iodine into iodic acid according to the reaction,

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O ?$$

(*a*) 12.4 g (*b*) 24.8 g (*c*) 0.248 g (*d*) 49.6 g

42. How much Cl_2 at STP is liberated when 1 mole $KMnO_4$ reacts with HCl?
(*a*) 11.2 L (*b*) 22.4 L (*c*) 44.8 L (*d*) 56 L

43. 27 g of Al will react completely with how many grams of oxygen?
(*a*) 8 g (*b*) 16 g (*c*) 32 g (*d*) 24 g

44. If 0.50 mole of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is:
(*a*) 0.70 (*b*) 0.50 (*c*) 0.20 (*d*) 0.10

45. 0.5 mole of H_2SO_4 is mixed with 0.2 mole of $Ca(OH)_2$. The maximum number of moles of $CaSO_4$ formed is:
(*a*) 0.2 (*b*) 0.5 (*c*) 0.4 (*d*) 1.5

Prabal (JEE Main Level)

1. A sample of calcium phosphate $Ca_3(PO_4)_2$ contains 8 mol of O atoms. The number of mole of Ca atoms in the sample is:
(*a*) 4 (*b*) 1.5 (*c*) 3 (*d*) 8

2. Ratio of masses of H_2SO_4 and $Al_2(SO_4)_3$ each containing 32 grams of S is ________.
(*a*) 0.86 (*b*) 1.72 (*c*) 0.43 (*d*) 2.15

3. Which has maximum number of atoms of oxygen?
(*a*) 10 ml $H_2O(l)$
(*b*) 0.1 mole of V_2O_5
(*c*) 12 gm $O_3(g)$
(*d*) 12.044×10^{22} molecules of CO_2

4. Mass of one atom of the element A is 3.9854×10^{-23}g. How many atoms are contained in 1g of the element A?
(*a*) 2.509×10^{22} (*b*) 6.022×10^{23}
(*c*) 12.044×10^{23} (*d*) None of these

5. The number of atoms present in 0.5 g-atoms of nitrogen is same as the atoms in:
(*a*) 12 g of C (*b*) 32 g of S
(*c*) 8 g of oxygen (*d*) 24 g of Mg

6. How many moles of magnesium phosphate $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms?
(*a*) 0.02 (*b*) 3.125×10^{-2}
(*c*) 1.25×10^{-2} (*d*) 2.5×10^{-2}

7. 64 g of an organic compound has 24 g carbon and 8 g hydrogen and the rest is oxygen. The empirical formula of the compound is:
(*a*) CH_4O (*b*) CH_2O
(*c*) C_2H_4O (*d*) None of these

8. Two elements X (atomic mass = 75) and Y (atomic mass = 16) combine to give a compound having 75.8% of X. The formula of the compound is:
(*a*) X_2Y_3 (*b*) X_2Y (*c*) X_2Y_2 (*d*) XY

9. A definite amount of gaseous hydrocarbon was burnt with just sufficient amount of O_2. The volume of all reactants was 600 ml, after the explosion the volume of the products [$CO_2(g)$ and $H_2O(g)$] was found to be 700 ml under the similar conditions. The possible molecular formula of the compound is:
(*a*) C_3H_8 (*b*) C_3H_6 (*c*) C_3H_4 (*d*) C_4H_{10}

10. Mole fraction of ethyl alcohol in aqueous ethyl alcohol (C_2H_5OH) solution is 0.25. Hence, percentage of ethyl alcohol by weight is:
(*a*) 54% (*b*) 25%
(*c*) 75% (*d*) 46%

11. 74 gm of sample on complete combustion gives 132 gm CO_2 and 54 gm of H_2O. The molecular formula of the compound may be:
(*a*) C_5H_{12} (*b*) $C_4H_{10}O$
(*c*) $C_3H_6O_2$ (*d*) $C_3H_7O_2$

12. Weight of oxygen in Fe_2O_3 and FeO in the simple ratio for the same amount of iron, is:
(*a*) 3 : 2 (*b*) 1 : 2
(*c*) 2 : 1 (*d*) 3 : 1

13. A person needs on average of 2.0 mg of riboflavin (vitamin B_2) per day. How many gm of butter should be taken by the person per day if it is the only source of riboflavin? (Butter contains 5.5 microgram riboflavin per gm.)
(*a*) 363.6 gm (*b*) 2.75 mg
(*c*) 11 gm (*d*) 19.8 gm

14. The oxide of a metal contains 30% oxygen by weight. If the atomic ratio of metal and oxygen is 2 : 3, determine the atomic weight of metal.
(*a*) 12 u (*b*) 56 u (*c*) 27 u (*d*) 52 u

15. When a mixture of 10 mole of SO_2 and 15 mole of O_2 was passed over catalyst, 8 mole of SO_3 was formed. How many mole of SO_2 and O_2 did not enter into combination?
(*a*) 2 moles of SO_2, 11 moles of O_2
(*b*) 3 moles of SO_2, 11.5 moles of O_2
(*c*) 2 moles of SO_2, 4 moles of O_2
(*d*) 8 moles of SO_2, 4 moles of O_2

16. $C_6H_5OH(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
Magnitude of volume change if 30 ml of C_6H_5OH (g) is burnt with excess amount of oxygen, is:
(*a*) 30 ml (*b*) 60 ml
(*c*) 20 ml (*d*) 10 ml

17. Mass of sucrose $C_{12}H_{22}O_{11}$ produced by mixing 84 gm of carbon, 12 gm of dihydrogen and 56 lit. O_2 at 1 atm & 273 K according to given reaction, is:
$C(s) + H_2(g) + O_2(g) \rightarrow C_{12}H_{22}O_{11}(s)$
(*a*) 138.5 (*b*) 155.5
(*c*) 172.5 (*d*) 199.5

18. What volume (in ml) of 0.2 M H_2SO_4 solution should be mixed with the 40 ml of 0.1 M NaOH solution such that the resulting solution has the concentration of H_2SO_4 as $\frac{6}{55}$ M.
(*a*) 70 (*b*) 45
(*c*) 30 (*d*) 58

19. For the reaction; $2x + 3y + 4z \rightarrow 5w$, initially 1 mol of x, 3 mol of y and 4 mol of z is taken. If 1.25 mol of w is obtained then % yield of this reaction is:
(*a*) 50% (*b*) 60%
(*c*) 70% (*d*) 40%

20. If 10 g of Ag reacts with 1 g of sulphur, the amount of Ag_2S formed will be:

(*a*) 7.75 g (*b*) 0.775 g

(*c*) 11 g (*d*) 10 g

21. A solution of A (MM = 20) and B (MM = 10), [Mole fraction $X_B = 0.6$] has density 0.7 gm/ml then molarity and molality of B in this solution will be ________ and ________ respectively.

(*a*) 30 M, 75 m

(*b*) 40 M, 75 m

(*c*) 30 M, 65 m

(*d*) 50 M, 55 m

22. 125 ml of 8% w/w NaOH solution (sp. gravity = 1) is added to 125 ml of 10 % w/v HCl solution. The nature of resultant solution would be ________.

(*a*) Acidic (*b*) Basic

(*c*) Neutral (*d*) None of these

23. 36.5 % (w/w) HCl has density equal to 1.20 g mL^{-1}. The molarity (M) and molality (m), respectively, are:

(*a*) 15.7, 15.7 (*b*) 12, 12

(*c*) 15.7, 12 (*d*) 12, 15.7

24. An aqueous solution of ethanol has density 1.025 g/mL and it is 2 M. What is the molality of this solution?

(*a*) 1.79 (*b*) 2.143

(*c*) 1.951 (*d*) None of these.

25. 500 mL of a glucose solution contains 6.02×10^{22} molecules of glucose. The concentration of the solution is:

(*a*) 0.1 M (*b*) 1.0 M

(*c*) 0.2 M (*d*) 2.0 M

26. Equal moles of H_2O and NaCl are present in a solution. Hence, molality of NaCl solution is:

(*a*) 0.55 (*b*) 55.5

(*c*) 1.00 (*d*) 0.18

27. Decreasing order of mass of pure NaOH in each of the aqueous solution.

I. 50 g of 40% (w/w) NaOH

II. 50 ml of 50% (w/v) NaOH ($d_{sol} = 1.2$ g/ml).

III. 50 g of 15 M NaOH ($d_{sol} = 1$ g/ml).

(*a*) I, II, III (*b*) III, II, I

(*c*) II, III, I (*d*) III = II = I

28. A solution of $FeCl_3$ is $\frac{M}{30}$, its molarity for Cl^- ion will be:

(*a*) $\frac{M}{90}$ (*b*) $\frac{M}{30}$

(*c*) $\frac{M}{10}$ (*d*) $\frac{M}{5}$

29. What volume of a 0.8 M solution contains 100 milli moles of the solute?

(*a*) 100 mL (*b*) 125 mL

(*c*) 500 mL (*d*) 62.5 mL

30. 4.4 g of CO_2 and 2.24 litre of H_2 at STP are mixed in a container. The total number of molecules present in the container will be:

(*a*) 6.022×10^{23} (*b*) 1.2046×10^{23}

(*c*) 6.022×10^{22} (*d*) 6.022×10^{24}

31. 10 g of $CaCO_3$ on heating gives 5 g of the residue (as CaO). The percent yield of the reaction is approximately:

(*a*) 50% (*b*) 72% (*c*) 89% (*d*) 100%

32. 33.6 g of an impure sample of sodium bicarbonate when heated strongly gave 4.4 g of CO_2. The percentage purity of $NaHCO_3$ would be:

(*a*) 25% (*b*) 50%

(*c*) 75% (*d*) 100%

33. A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by weight. Therefore the ratio of their number of molecules is:

(*a*) 1 : 4 (*b*) 1 : 8

(*c*) 7 : 32 (*d*) 3 : 16

34. 2.76 g of silver carbonate on being strongly heated yields a residue weighing:

(*a*) 2.16 g (*b*) 2.48 g

(*c*) 2.32 g (*d*) 2.64 g

35. 12 g of alkaline earth metal gives 14.8 g of its nitride. Atomic weight of metal is:

(*a*) 12 (*b*) 20

(*c*) 40 (*d*) 14.8

36. How many liters of CO_2 at STP will be formed when 0.01 mol of H_2SO_4 reacts with excess of Na_2CO_3.

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$$

(*a*) 22.4 L (*b*) 2.24 L

(*c*) 0.224 L (*d*) 1.12 L

37. Equal weight of 'X' (At. wt. = 36) and 'Y' (At. wt. = 24) are reacted to form the compound X_2Y_3. Then

(*a*) X is the limiting reagent

(*b*) Y is the limiting reagent

(*c*) No reactant is left over and mass of X_2Y_3 formed is double the mass of 'X' taken

(*d*) None of these

38. A person adds 1.71 gram of sugar ($C_{12}H_{22}O_{11}$) in order to sweeten his tea. The number of carbon atoms added are (mol. mass of sugar = 342)

(*a*) 3.6×10^{22} (*b*) 7.2×10^{21}

(*c*) 0.05×10^{20} (*d*) 6.6×10^{22}

39. A compound contains 38.8 % C, 16.0 % H and 45.2 % N. The formula of the compound would be

(*a*) CH_3NH_2 (*b*) CH_3CN

(*c*) C_2H_5CN (*d*) $CH_2(NH)_2$

40. When 100 g of ethylene polymerises entirely to polyethene, the weight of polyethene formed as per the equation $n(C_2H_4) \longrightarrow (-CH_2-CH_2-)_n$ is:

(*a*) (n/2)g (*b*) 100g

(*c*) (100/n)g (*d*) 100ng

41. What is the concentration of nitrate ions if equal volumes of 0.1 M $AgNO_3$ and 0.1 M NaCl are mixed together?

(*a*) 0.1 N (*b*) 0.2 M

(*c*) 0.05 M (*d*) 0.25 M

42. 0.16 g of dibasic acid required 25 ml of M/10 NaOH for complete neutralization. Molecular weight of acid is:

(*a*) 32 (*b*) 64

(*c*) 128 (*d*) 256

43. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 M NaOH required to completely neutralize 10 ml of this solution is:

(*a*) 40 ml (*b*) 20 ml

(*c*) 10 ml (*d*) 4 ml

44. Which of the following contains the greatest number of oxygen atoms?

(*a*) 1g of O (*b*) 1g of O_2

(*c*) 1g of O_3 (*d*) All same

45. For sequential reaction :

$$A \longrightarrow B + C \qquad ...(i)$$

$$2B \longrightarrow C + 2D \qquad ...(ii)$$

If % yield of (i) and (ii) reactions are 90% and 80% respectively then the overall % yield is expected to be:

(*a*) 90% (*b*) 80% (*c*) 72% (*d*) 10%

46. If 32 g of O_2 contains 6.022×10^{23} molecules at STP then 32 g of S, under the same conditions, will contain,

(*a*) 6.022×10^{23} S atoms (*b*) 3.011×10^{23} S atoms

(*c*) 12.044×10^{23} S atoms (*d*) 1×10^{23} S atoms

INTEGER TYPE QUESTIONS

47. The specific gravity of a solution is 1.8, having 62% by weight of acid. It is to be diluted to specific gravity of 1.2. What volume of water (in mL) should be added to 100 ml of this solution?

48. Carbon disulphide, CS_2, can be made from by-product SO_2. The overall reaction is

$$5C + 2SO_2 \longrightarrow CS_2 + 4CO$$

How much CS_2 (in kg) can be produced from 440 kg of waste SO_2 with 60 kg of coke if the SO_2 conversion is 80%?

49. Pure iron pyrite, FeS_2, is burnt with 50% excess air than required for complete oxidation of FeS_2, in a closed vessel.

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Air contains 20% O_2 and 80% N_2, by volume. The mole percent of N_2 gas in the gaseous mixture, after complete reaction, is.

50. An element A forms both a dichloride (ACl_2) and a tetrachloride (ACl_4). Treatment of 27.8 g ACl_2 with excess chlorine forms 34.9 g ACl_4. Then atomic mass (in g/mol) of 'A' is:

51. Mixture of 10 moles of Fe_2S_3, 20 moles of H_2O and 30 mole of O_2 react with 30% yield of given reaction:

$$Fe_2S_3 + H_2O + O_2 \rightarrow Fe(OH)_3 + S$$

Calculate moles of $Fe(OH)_3$ that can be produced in above reaction.

52. Sample of an element "X" consist of its three isotopes A_1, A_2 & A_3 and population of A_2 is three times the population of A_3. If the average molar mass of sample is 1.25, determine percentage population of A_1 (Molar masses of isotopes A_1, A_2 & A_3 are 1, 2 and 3 gm/mol respectively.)

53. A solution of A (MM=20) and B (MM= 10), [Mole fraction $X_B = 0.6$] has density 0.7 gm/ml then molarity and molality of B in this solution will be ______M and _____m respectively.

54. A piece of aluminium weighing 2.7 g is heated with 75.0 ml of H_2SO_4 (sp. gr. 1.2 containing 25% H_2SO_4 by mass). After the metal is completely dissolved, the solution is diluted to 400ml. What is the molarity of the free H_2SO_4 in the resulting solution (Multiply final answer by 10)?

55. The odour of skunk is caused by chemical compounds called thiols ($C_4H_{10}S$). These can be deodorized by reaction with household bleach (NaOCl) according to following unbalanced reaction:

$$C_4H_{10}S + NaOCl(aq) \rightarrow C_8H_{18}S_2 + NaCl(aq) + H_2O(aq)$$

How many gram of thiol can be deodorized by 74.5 gm of NaOCl?

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. (i) $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

(ii) $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$

(iii) $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$

Above series of reactions are carried out starting with 18 g of Al and 109.5 g of HCl in first step and further 100 g of NaOH is added for step (ii) and (iii). Find out limiting reagent in each step and calculate the maximum amount of $NaAlO_2$ that can be produced in step (iii). (Assume reactions are taken in sequence and also that each reaction goes to 100% completion)

	L.R. in step (I)	L.R. in step (II)	L.R. in step (III)	Moles of $NaAlO_2$
(*a*)	Al	$AlCl_3$	$Al(OH)_3$	0.66
(*b*)	Al	Na(OH)	$Al(OH)_3$	0.5
(*c*)	Al	$AlCl_3$	NaOH	0.5
(*d*)	HCl	$AlCl_3$	NaOH	0.5

2. A mixture of CH_4 and C_2H_2 was completely burnt in an excess of oxygen yielding equal volumes of CO_2 and steam, measured at the same temperature and pressure. The mole percent of CH_4 in the original mixture is

(*a*) 25% (*b*) 30%
(*c*) 75% (*d*) 50%

3. The strength of 10^{-2} M Na_2CO_3 solution in terms of molality will be (density of solution = 1.10 g mL^{-1}). (Molecular weight of Na_2CO_3 = 106 g mol^{-1})

(*a*) 9.00×10^{-3} (*b*) 1.5×10^{-2}
(*c*) 5.1×10^{-3} (*d*) 11.2×10^{-3}

4. 10 moles of X, 12 mole of Y and 20 moles of Z are mixed to produce a final product P, according to the given balanced reactions:

$$X + 2Y \longrightarrow I$$
$$I + Z \longrightarrow Y + P$$

then the maximum no. of moles of P, which can be produced assuming that the products formed can also be reused in the reaction?

(*a*) 6 mole (*b*) 9 mole
(*c*) 10 mole (*d*) 12 mole

5. A compound contains 4% oxygen, $\frac{14}{3}$% nitrogen, 4% sulphur. Then empirical formula of compound contains ________ number of nitrogen atoms.

(*a*) 6 (*b*) 8
(*c*) 3 (*d*) Can not be determined

6. 56 gm of N_2 and 9 gm of H_2 are made to react completely to produce a mixture of NH_3 and N_2H_4. The ratio of moles of NH_3 and N_2H_4 is:

(*a*) 1 : 1 (*b*) 3 : 2
(*c*) 2 : 3 (*d*) None of these

7. 100 gm of an oleum sample (labelled as 109%) is mixed with 300 gm of another oleum sample (labelled as 118%). The new labelling of resulting oleum sample becomes

(*a*) 115.75% (*b*) 106.75%
(*c*) 163% (*d*) 15.75%

8. Iodobenzene is prepared from aniline ($C_6H_5NH_2$) in a two-step process as shown here.

$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$

$C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + N_2 + KCl$

In an actual preparation, 9.30 g of aniline was converted to 16.32 g of iodobenzene. The percentage yield of iodobenzene is (I = 127)

(*a*) 8% (*b*) 50%
(*c*) 75% (*d*) 80%

9. A protein isolated from a bovine preparation, was subjected to amino acid analysis. The amino acid present in the smallest amount was lysine, $C_6H_{14}N_2O_2$ and the amount of lysine was found to be 365 mg per 100 g protein. What is the minimum molecular mass (in g/mol) of the protein?

(*a*) 40,000,000 (*b*) 40,000
(*c*) 40 (*d*) 4,00,000

10. NX is produced by the following step of reactions:

$M + X_2 \rightarrow MX_2$,

$MX_2 + X_2 \rightarrow M_3X_8$,

$M_3X_8 + N_2CO_3 \rightarrow NX + CO_2 + M_3O_4$

How much M (metal) is consumed to produce 206 g of NX. (Take at wt. of M = 56, N = 23, X = 80)

(*a*) 42 g (*b*) 56 g (*c*) $\frac{14}{3}$ (*d*) $\frac{7}{4}$

11. Calculate percentage change in M_{avg} of the mixture, if PCl_5 undergo 50% decomposition.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

(*a*) 50% (*b*) 66.66 % (*c*) 33.33 % (*d*) Zero

12. An ore of iron contains FeS and some non-volatile impurity. Roasting of this ore converts all FeS into Fe_2O_3 and 4% loss in weight was observed. Mass percentage of FeS in ore will be

$$2FeS + \frac{7}{2}O_2 \longrightarrow Fe_2O_3 + 2SO_2$$

(*a*) 60 % (*b*) 44 % (*c*) 30 % (*d*) 66 %

13. Elements X and Y can combine to form two different compounds. If 1.6 g of X reacts with exactly 1.6 g of Y the compound produced has formula XY_2. However under different conditions, 2.4 g of X will react with 1.6 g of Y to form a second compound, whose empirical formula is ____.

(*a*) X_3Y_4 (*b*) XY (*c*) XY_3 (*d*) X_2Y

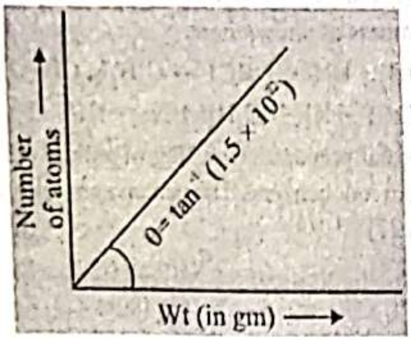
14. For a sequential reaction, $NH_3 \longrightarrow N_2 + H_2$ .....(i)

$H_2 + O_2 \longrightarrow H_2O$ ...(ii)

What will be the amount of water obtained if 5 moles of NH_3 is mixed with 3 moles of O_2 & % yield of 1st & 2nd reaction is 50% & 80% respectively?

(*a*) 3 moles (*b*) 2.5 mole
(*c*) 2 moles (*d*) 2.4 moles

15. A graph is plotted for an element by putting its mass on X-axis and the corresponding number of atoms on Y-axis. What is the atomic mass of the element for which the graph is plotted? ($N_A = 6.0 \times 10^{23}$)



(*a*) 80 (*b*) 40 (*c*) 0.025 (*d*) 20

16. On heating $KClO_3$ at a certain temperature, it is observed that one mole of $KClO_3$ yields one mole of O_2. What is the mole fraction of $KClO_4$ in the final solid mixture containing only KCl and $KClO_4$, the latter being formed by parallel reaction?

(*a*) 0.75 (*b*) 0.33
(*c*) 0.25 (*d*) 0.67

17. A drug, marijuana, owes its activity to tetrahydrocannabinol, which contains 70 percent as many carbon atoms as hydrogen atoms and 15 times as many hydrogen atoms as oxygen atoms. The number of moles in a gram of terahydrocannabinol is 0.00318. Determine its molecular formula.

(*a*) CH_3O_2 (*b*) $C_{21}H_{30}O_2$
(*c*) $C_{15}H_{30}O_2$ (*d*) $C_{70}H_{15}O$

18. From the following reactions,

$2CoF_2 + F_2 \rightarrow 2CoF_3$

$(CH_2)_n + 4n\, CoF_3 \rightarrow (CF_2)_n + 2n\, HF + 4n\, CoF_2$

Calculate how much F_2 will be consumed to produce 1 kg of $(CF_2)_n$. (F = 19)?

(*a*) 1.52 kg (*b*) 2.04 kg
(*c*) 0.76 kg (*d*) 4.56 kg

19. Hydrogen cyanide, HCN, can be made by a two step process. First, ammonia is reacted with O_2 to give nitric oxide, NO.

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Then nitric oxide is reacted with methane, CH_4.

$2NO(g) + 2CH_4(g) \rightarrow 2HCN(g) + 2H_2O(g) + H_2(g)$

When 25.5 g of ammonia and 32.0 g of methane are used, how much grams of hydrogen cyanide can be produced?

(*a*) 1.5 (*b*) 2.0 (*c*) 40.5 (*d*) 54.0

MULTIPLE CORRECT TYPE QUESTIONS

20. Which is/are correct statements about 1.7 g of NH_3?

(*a*) It contain 0.3 mol H – atoms.
(*b*) It contain 2.408×10^{23} atoms.
(*c*) Mass % of hydrogen is 17.65%.
(*d*) It contains 0.3 mol N-atoms.

21. If 27 g of carbon is mixed with 88 g of oxygen and is allowed to burn to produce CO_2, then:

(*a*) Oxygen is the limiting reagent.
(*b*) Volume of CO_2 gas produced at STP is 50.4 L.
(*c*) C and O combine in mass ratio of 3.8.
(*d*) Volume of unreacted O_2 at STP is 11.2 L.

22. For the following reaction : $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

106.0 g of Na_2CO_3 reacts with 109.5 g of HCl.

Which of the following is/are correct?

(*a*) The HCl is in excess amount.
(*b*) 117.0 g of NaCl is formed.
(*c*) The volume of CO_2 produced at NTP is 22.4 L.
(*d*) None of these

23. A sample of a mixture of $CaCl_2$ and NaCl weighing 4.44 g was treated to precipitate all the Ca as $CaCO_3$, which was then heated and quantitatively converted to 1.12 g of CaO. (At . wt. Ca = 40, Na = 23, Cl = 35.5)

(*a*) Mixture contains 50% NaCl by mass
(*b*) Mixture contains 60% $CaCl_2$ by mass
(*c*) Mass of $CaCl_2$ is 2.22 g in the mixture
(*d*) Mass of $CaCl_2$ is 1.11 g in the mixture

24. $A + B \rightarrow A_3B_2$ (unbalanced)

$A_3B_2 + C \rightarrow A_3B_2C_2$ (unbalanced)

Above two reactions are carried out by taking 3 moles each of A and B and one mole of C. Then, which option is/are correct?

(*a*) 1 mole of $A_3B_2C_2$ is formed.
(*b*) 1/2 mole of $A_3B_2C_2$ is formed.
(*c*) 1/2 mole of A_3B_2 is formed.
(*d*) 1/2 mole of A_3B_2 is left finally.

25. The **incorrect** statement(s) regarding 2 M $MgCl_2$ aqueous solution is/are: ($d_{solution} = 1.09$ gm/ml)

(*a*) Molality of Cl^- is 4.44 m.
(*b*) Mole fraction of $MgCl_2$ is approximately 0.035.
(*c*) The conc. of $MgCl_2$ is 19% w/v. (approx)
(*d*) The conc. of $MgCl_2$ is 19×10^4 ppm.

26. Solution containing 23 g HCOOH is/are:

(*a*) 46 g of 70% $\left(\frac{w}{v}\right)$ HCOOH ($d_{solution} = 1.40$ g/mL)
(*b*) 50 g of 10 M HCOOH ($d_{solution} = 1$ g/mL)
(*c*) 50 g of 25% $\left(\frac{w}{w}\right)$ HCOOH
(*d*) 46 g of 5 M HCOOH ($d_{solution} = 1$ g/mL)

27. A student was carrying out the following chemical reaction in Lab

$$2A + 3B \longrightarrow 6C \text{ (balanced reaction)}$$

He used 30 mole of A and 30 mole of B and at the end of reaction he found 40 moles of C were formed. Identify the correct statement(s).

(*a*) Total mass before and after the reaction will remain same.
(*b*) B is limiting reagent
(*c*) % yield is 60.
(*d*) At 50% yield 30 moles of C will be formed.

28. Which of the following contain same number of entities?

(*a*) Number of atoms in 1 mole $CuSO_4 \cdot 5H_2O$
(*b*) Number of neutrons in 3.5 mole of CH_4
(*c*) Number of atoms in 2 mole of $FeCr_2O_4$
(*d*) Number of electrons in 2.1 mole of NH_4^+

29. The non - stoichiometric compound, titanium monoxide, has a continuous range of composition from $Ti_{0.75}O$ to $TiO_{0.69}$. Which of the following is/are correct regarding the possible composition of the compound? [Ti = 48]

(*a*) The maximum percentage by mass of oxygen in the compound is 30.8.
(*b*) The minimum percentage by mass of titanium in the compound is 69.2.
(*c*) The minimum percentage by mass of oxygen in the compound is 18.7
(*d*) The minimum percentage by mass of titanium in the compound is 81.3.

30. For the following reaction;

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Identify the compositions which will produce same amount of NH_3.

(*a*) 140 g N_2 & 35 g H_2
(*b*) 18 g H_2 & 52 g N_2
(*c*) Total 20 moles of mixture having N_2 & H_2 present in stoichiometric ratio (No limiting reagent).
(*d*) 136 gm of mixture having mass fraction of $H_2 = \frac{6}{34}$.

31. Which of the following solution contains same molar concentration?

(*a*) 166 g KI per liter solution
(*b*) 33.0 g $(NH_4)_2SO_4$ in 200 mL solution
(*c*) 25.0 g $CuSO_4.5H_2O$ in 100 mL solution
(*d*) 27.0 mg Al^{3+} per mL solution

32. If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 9.8%(w/w) H_2SO_4 solution (d = 1 g/mL), then:

(*a*) Concentration of solution remains same.
(*b*) Volume of solution become 200 mL.
(*c*) Mass of H_2SO_4 in the final solution is 98 g.
(*d*) Mass of H_2SO_4 in the final solution is 19.6 g.

33. Aspartame is an artificial sweetener that is 160 times sweeter than sucrose (table sugar). It is marketed as Nutra sweet. Its molecular formulae is $C_{14}H_{18}N_2O_5$. If its 5 gm molecule are taken then which of the following is/are correct?

(*a*) Mass of hydrogen is 90 gm.
(*b*) Ratio of mass of carbon to oxygen = 2.1
(*c*) Contain 5 gm atom of oxygen.
(*d*) Contain 159 mole of total atoms.

34. $X + Y \longrightarrow X_3Y_4$. This reaction is carried out by taking 6 moles each of X and Y respectively then

(*a*) X is the limiting reagent
(*b*) 1.5 moles of X_3Y_4 is formed
(*c*) 1.5 moles of excess reagent is left behind
(*d*) 75% of excess reagent reacted

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 35 to 37): A chemist decided to determine the molecular formula of an unknown compound. He collects following informations:

I. Compound contain 2 : 1 'H' to 'O' atoms (number of atoms).
II. Compound has 40% C by mass.
III. Approximate molecular mass of the compound is 178 g.
IV. Compound contains C, H and O only.

35. What is the % by mass of oxygen in the compound?

(*a*) 53.33% (*b*) 88.88%
(*c*) 33.33% (*d*) None of these

36. What is the empirical formula of the compound?

(*a*) CH_3O (*b*) CH_2O (*c*) C_2H_2O (*d*) CH_3O_2

37. Which of the following could be molecular formula of compound?

(*a*) $C_6H_6O_6$ (*b*) $C_6H_{12}O_6$
(*c*) $C_6H_{14}O_{12}$ (*d*) $C_6H_{14}O_6$

Comprehension (Q. 38 to 40): Oleum is considered as a solution of SO_3 in H_2SO_4, which is obtained by passing SO_3 in solution of H_2SO_4. When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is known as % labelling in oleum.

For example, a oleum bottle labelled as 109% H_2SO_4 means the 109g total mass of pure H_2SO_4 will be formed when 100 g of oleum is diluted by 9 g of H_2O which combines with all the free SO_3 to form H_2SO_4 as

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

38. What is the % of free SO_3 in an oleum that is labelled as '104.5% H_2SO_4'?

(*a*) 10 (*b*) 20
(*c*) 40 (*d*) None of these

39. If excess water is added into a 100 g bottle sample labelled as 112% H_2SO_4 and is reacted with 5.3g Na_2CO_3, then find the volume of CO_2 evolved at 1 atm pressure and 300 k temperature after the completion of the reaction: [R = 0.0821 L atom mol^{-1} K^{-1}]

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

(*a*) 2.46 L (*b*) 24.6 L (*c*) 1.23 L (*d*) 123

40. 1g of oleum sample is diluted with water. The solution required 54 ml of 0.4 N NaOH for compete neutralisation. The % of free SO_3 in the sample is:

(*a*) 74 (*b*) 26

(*c*) 20 (*d*) None of these

Comprehension (Q. 41 to 43): According to the Avogadro's law, equal number of moles of gases occupy the same volume at identical condition of temperature and pressure.

Now let us assume air to consist of 80% by volume of nitrogen (N_2) and 20% by volume of oxygen (O_2). If air is taken at STP, then its 1 mol would occupy 22.4 L. 1 mol of air would contain 0.8 mol of N_2 and 0.2 mol of O_2, hence the mole fractions of N_2 and O_2 are given by $X_{N_2} = 0.8$ and $X_{O_2} = 0.2$.

41. Volume occupied by air at STP containing exactly 11.2 g of nitrogen, is:

(*a*) 22.4 L (*b*) 8.96 L

(*c*) 11.2 L (*d*) 2.24 L

42. If air is treated as a solution of O_2 and N_2, then % w/w of oxygen is:

(*a*) $\frac{10}{9}$ (*b*) $\frac{200}{9}$

(*c*) $\frac{700}{9}$ (*d*) $\frac{350}{9}$

43. Density of air at STP is:

(*a*) 1 g/L (*b*) $\frac{9}{7}$ g/L

(*c*) $\frac{2}{7}$ g/L (*d*) Can't be determined

MATCH THE COLUMN TYPE QUESTIONS

44.

	Column-I		Column-II
A.	100 mL of 0.2 M $AlCl_3$ solution + 400 ml of 0.1 M HCl solution	p.	Total concentration of cation(s) = 0.12 M
B.	50 mL of 0.4 M KCl + 50 ml H_2O	q.	$[SO_4^{2-}] = 0.06$ M
C.	30 mL of 0.2 M K_2SO_4 + 70 ml H_2O	r.	$[SO_4^{2-}] = 2.5$ M
D.	200 mL 24.5% (w/v) H_2SO_4	s.	$[Cl^-] = 0.2$ M

(*a*) A → r,s; B → s; C → p,q; D → r

(*b*) A → p,s; B → s; C → p,q; D → r

(*c*) A → p,s; B → s; C → s,q; D → r

(*d*) A → p,s; B → p,s; C → p,q; D → r

45.

	Column-I		Column-II
A.	A gaseous organic compound containing C = 52.17%, H = 13.04% & O = 34.78% (by weight) having molar mass 46 g/mol.	p.	One mole of compound contains $4N_A$ atoms of hydrogen.
B.	0.3 g of an organic compound containing C, H and O on combustion yields 0.44 g of CO_2 and 0.18 g of H_2O, and two O per molecule	q.	The empirical formula of the compound is same as its molecular formula.
C.	A hydrocarbon containing C = 42.857% and H = 57.143% (by mole) and 3C atoms per molecule.	r.	Combustion products of one mole of compound contains larger number of moles of CO_2 than that of H_2O.
D.	A hydrocarbon containing 10.5 g carbon per gram of hydrogen and having vapour density 46.	s.	CO_2 gas produced by the combustion of 0.25 mole of compound occupies a volume of 11.2 L at STP.

(*a*) A → p,r; B → q,s; C → p,q; D → q,r,s

(*b*) A → q,s; B → r,s; C → p,q,r; D → q,p

(*c*) A → r,p; B → q,r,p; C → r,s; D → q,r

(*d*) A → q,s; B → p,s; C → p,q,r; D → q,r

NUMERICAL TYPE QUESTIONS (UPTO ONE DECIMAL)

46. Nitric acid can be produced from ammonia in three step process.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \quad ...(i)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad ...(ii)$$

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq.) + NO(g) \quad ...(iii)$$

Calculate weight of NH_3 (in kg) required to produce 1260 kg of HNO_3. (When % yield of 1st, 2nd and 3rd reaction are respectively 69%, 60% and 68% respectively.)

47. CS_2 and Cl_2 in the weight ratio 1 : 2 are allowed to react according to equation $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$. Find the fraction of excess reagent left behind:

48. Haemoglobin contains 0.25% Iron by weight. The molar mass of Haemoglobin is 89600. Calculate the weight(in g) of $K_4[Fe(CN)_6]$ that can be produced if all the iron atoms from 4.48 kg Haemoglobin are converted into $K_4[Fe(CN)_6]$ through a series of reactions.

[molar mass of $K_4[Fe(CN)_6] = 368$]

INTEGER TYPE QUESTIONS

49. A solution contain substances A and B in H_2O (solvent). The mole fraction of 'A' is 0.05 and molarity of 'B' is 7 M. The solution has density 1.14 gm/ml. Calculate "molarity of A". [Molecular weight of A = 10 gm/mol; molecular weight of B = 30 gm/mol]

50. A fluorine disposal plant was constructed to carryout the following reactions:

$$F_2 + 2NaOH \longrightarrow \frac{1}{2}O_2 + 2NaF + H_2O$$

$$2NaF + CaO + H_2O \longrightarrow CaF_2 + 2NaOH$$

Over a period of operation, 1900 kg of fluorine was fed into a plant and 10,000 kg of lime was required. What was the percentage utilisation of lime ? [Lime : CaO]

51. Based on the following information, determine sum of value of x and y:

$$(CH_3)_xAlCl_y(0.643g) \longrightarrow xCH_4(g)(0.22\text{ g}) + yCl^- + Al^{3+}$$

$$\xrightarrow{AgNO_3} \text{white ppt. } (0.996g).$$

52. A mixture of $NH_3(g)$ & $N_2H_4(g)$ is placed in a sealed container at 300K. The total pressure is 0.5 atm. The container is heated to 1200 K at which time both substances decompose completely according to the equations

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$ and

$N_2H_4(g) \longrightarrow N_2(g) + 2H_2(g)$

After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. Find the mole % of NH_3 in the original mixture.

53. In a container 6 litre N_2 and 30 litre H_2 is taken which react according to the following reactions and N_2H_2 reacts with H_2 to give N_2H_4.

$N_2(g) + H_2(g) \longrightarrow N_2H_2(g)$

$N_2H_2(g) + H_2(g) \longrightarrow N_2H_4(l)$

Find percentage of volume contracted.

54. Atoms of elements A, B and C combine to form a compound in the atomic ratio of 1: 6: 2. Atomic masses of A, B and C are 64, 4 and 16, respectively. Calculate the maximum mass (in mg) of the compound formed from1.28 gm of A, 3.0×10^{23} atoms of B and 0.04 mole atom of C. [Take: $N_A = 6 \times 10^{23}$]

55. $KClO_4$ can be prepared by Cl_2 and KOH by a series of reactions as given below:

$Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O$

$3KClO \longrightarrow 2KCl + KClO_3$

$4KClO_3 \longrightarrow 3KClO_4 + KCl$

If 10 moles of Cl_2 are mixed with 22 moles of KOH then calculate total moles of all the substances at the end of reaction. (Assuming 100% yield of all the reactions.)

PYQ's (Past Year Questions)

PROPERTIES OF MATTER AND THEIR MEASUREMENT

1. The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 'A' × 10^{12} hertz and that has a radiant intensity in that direction of $\frac{1}{'B'}$ watt per steradian. 'A' and 'B' are respectively. **[09 April, 2024 (Shift-II)]**

(*a*) 540 and $\frac{1}{683}$ (*b*) 540 and 683

(*c*) 450 and $\frac{1}{683}$ (*d*) 450 and 683

UNCERTAINTY IN MEASUREMENT AND LAWS OF CHEMICAL COMBINATIONS

2. Which of the following have same number of significant figures? **[8 April, 2023 (Shift-II)]**

A. 0.00253 B. 1.0003

C. 15.0 D. 163

Choose the correct answer from the options given below

(*a*) A, B and C only (*b*) C and D only

(*c*) A, C and D only (*d*) B and C only

3. Using the rules for significant figures, the correct answer for the expression $\frac{0.02858 \times 0.112}{0.5702}$ **[29 June, 2022 (Shift-II)]**

(*a*) 0.005613 (*b*) 0.00561

(*c*) 0.0056 (*d*) 0.006

4. The number of significant figures in 50000.020×10^{-3} is______. **[26 Feb, 2021 (Shift-I)]**

5. To check the principle of multiple proportions, a series of pure binary compounds (P_mQ_n) were analyzed and their composition is tabulated below. The correct option(s) is(are) **[JEE Adv 2022]**

Compound	Weight % of P	Weight % of Q
1	50	50
2	44.4	55.6
3	40	60

(*a*) If empirical formula of compound 3 is P_3Q_4, then the empirical formula of compound 2 is P_3Q_5.

(*b*) If empirical formula of compound 3 is P_3Q_2 and atomic weight of element P is 20, then the atomic weight of Q is 45.

(*c*) If empirical formula of compound 2 is PQ, then the empirical formula of the compound 1 is P_5Q_4.

(*d*) If atomic weight of P and Q are 70 and 35, respectively, then the empirical formula of compound 1 is P_2Q.

DALTON'S ATOMIC THEORY

6. Choose the Incorrect Statement about Dalton's Atomic Theory **[04 April, 2024 (Shift-II)]**
   (*a*) Compounds are formed when atoms of different elements combine in any ratio
   (*b*) All the atoms of a given element have identical properties including identical mass
   (*c*) Matter consists of indivisible atoms
   (*d*) Chemical reactions involve reorganization of atoms

7. The incorrect postulates of the Dalton's atomic theory are:
   (A) Atoms of different elements differ in mass.
   (B) Matter consists of divisible atoms.
   (C) Compounds are formed when atoms of different element combine in a fixed ratio.
   (D) All the atoms of given element have different properties including mass.
   (E) Chemical reactions involve reorganisation of atoms.
   Choose the correct answer from the options given below: **[05 April, 2024 (Shift-I)]**
   (*a*) (B), (D), (E) only (*b*) (A), (B), (D) only
   (*c*) (C), (D), (E) only (*d*) (B), (D) only

ATOMIC & MOLECULAR MASSES

8. The average molar mass of chlorine is 35.5 g mol^{-1}. The ratio of ^{35}Cl to ^{37}Cl in naturally occurring chlorine is close to: **[6 Sept, 2020 (Shift-II)]**
   (*a*) 4 : 1 (*b*) 3 : 1 (*c*) 2 : 1 (*d*) 1 : 1

MOLE CONCEPT AND MOLAR MASSES

9. 0.05 cm thick coating of silver is deposited on a plate of 0.05 m^2 area. The number of silver atoms deposited on plate are __________ × 10^{23}. (At mass Ag = 108, d = 7.9 g cm^{-3}) **[30 Jan, 2024 (Shift-I)]**

10. Match List-I with List-II. **[10 April, 2023 (Shift-II)]**

List-I		List-II	
A.	16g of $CH_4(g)$	p.	Weighs 28 g
B.	1g of $H_2(g)$	q.	60.2 × 10^{23} electrons
C.	1 mole of $N_2(g)$	r.	Weighs 32g
D.	0.5 mol of $SO_2(g)$	s.	Occupies 11.4 L volume at STP

   Choose the correct answer from the options given below:
   (*a*) (A)-(p), (B)-(r), (C)-(q), (D)-(s)
   (*b*) (A)-(q), (B)-(r), (C)-(r), (D)-(p)
   (*c*) (A)-(q), (B)-(s), (C)-(r), (D)-(p)
   (*d*) (A)-(q), (B)-(s), (C)-(p), (D)-(r)

11. When 0.01 mol of an organic compound containing 60% carbon was burnt completely, 4.4 g of CO_2 was produced. The molar mass of compound is __________ g mol^{-1} (Nearest integer) **[29 Jan, 2023 (Shift-II)]**

12. Production of iron in blast furnace follows the following equation $Fe_3O_4(s) + 4CO(g) \longrightarrow 3Fe(l) + 4CO_2(g)$
    When 4.640 kg of Fe_3O_4 and 2.520 kg of CO are allowed to react then the amount of iron (in g) produced is:
    [Given: Molar Atomic mass (g mol^{-1}); Fe = 56
    Molar Atomic mass (g mol^{-1}); O = 16
    Molar Atomic mass (g mol^{-1}); C = 12]
    [29 June, 2022 (Shift-I)]
    (*a*) 1400 (*b*) 2200 (*c*) 3360 (*d*) 4200

13. 4g equimolar mixture of NaOH and Na_2CO_3 contains x g of NaOH and y g of Na_2CO_3. The value of x is __________ g. (Nearest Integer) **[20 July, 2021 (Shift-II)]**

14. $NaClO_3$ is used, even in spacecraft, to produce O_2. The daily consumption of pure O_2 by a person is 492L at 1 atm, 300 K. How much amount of $NaClO_3$, in grams, is required to produce O_2 for the daily consumption of a person at 1 atm, 300 K?
    $NaClO_3(s) + Fe(s) \rightarrow O_2(g) + NaCl(s) + FeO(s)$
    R = 0.082 L atm mol^{-1} K^{-1}. **[8 Jan, 2020 (Shift-II)]**

15. 5 moles of AB_2 weigh 125 × 10^{-3} kg and 10 moles of A_2B_2 weigh 300 × 10^{-3} kg. The molar mass of $A_{(M_A)}$ and molar mass of $B_{(M_B)}$ in kg mol^{-1} are: **[12 April, 2019 (Shift-I)]**
    (*a*) $M_A = 50 \times 10^{-3}$ and $M_B = 25 \times 10^{-3}$
    (*b*) $M_A = 25 \times 10^{-3}$ and $M_B = 50 \times 10^{-3}$
    (*c*) $M_A = 5 \times 10^{-3}$ and $M_B = 10 \times 10^{-3}$
    (*d*) $M_A = 10 \times 10^{-3}$ and $M_B = 5 \times 10^{-3}$

16. Aluminium reacts with sulfuric acid to form aluminium sulfate and hydrogen. What is the volume of hydrogen gas in liters (L) produced at 300 K and 1.0 atm pressure, when 5.4 g of aluminium and 50.0 mL of 5.0 M sulfuric acid are combined for the reaction?
    (Use molar mass of aluminium as 27.0 g mol^{-1}, R = 0.082 atm L mol^{-1} K^{-1}) **[JEE Adv 2020]**

PERCENTAGE COMPOSITION AND EMPIRICAL & MOLECULAR FORMULA

17. A sample of $CaCO_3$ and $MgCO_3$ weighed 2.21 g is ignited to constant weight of 1.152 g. The composition of mixture is:
    (Given molar mass in g mol^{-1} $CaCO_3$: 100, $MgCO_3$: 84)
    [31 Jan, 2024 (Shift-II)]
    (*a*) 1.187 g $CaCO_3$ + 1.023 g $MgCO_3$
    (*b*) 1.023 g $CaCO_3$ + 1.023 g $MgCO_3$
    (*c*) 1.187 g $CaCO_3$ + 1.187 g $MgCO_3$
    (*d*) 1.023 g $CaCO_3$ + 1.187 g $MgCO_3$

18. 10 mL of gaseous hydrocarbon on combustion gives 40 mL of $CO_2(g)$ and 50 mL of water vapour. Total number of carbon and hydrogen atoms in the hydrocarbon is _____.
    [01 Feb, 2024 (Shift-II)]

19. An organic compound has 42.1% carbon, 6.4% hydrogen and remainder is oxygen. If its molecular weight is 342, then its molecular formula is: **[05 April, 2024 (Shift-I)]**
    (*a*) $C_{11}H_{18}O_{12}$ (*b*) $C_{12}H_{20}O_{12}$
    (*c*) $C_{14}H_{20}O_{10}$ (*d*) $C_{12}H_{22}O_{11}$

20. When a hydrocarbon A undergoes combustion in the presence of air, it requires 9.5 equivalents of oxygen and produces 3 equivalents of water. What is the molecular formula of A? **[29 Jan, 2023 (Shift-II)]**

(*a*) C_8H_6 (*b*) C_9H_9 (*c*) C_6H_6 (*d*) C_9H_6

21. A metal chloride contains 55.0% of chlorine by weight. 100 mL vapours of the metal chloride at STP weigh 0.57 g. The molecular formula of the metal chloride is

(Given: Atomic mass of chlorine is 35.5 u) **[12 April, 2023 (Shift-I)]**

(*a*) MCl_2 (*b*) MCl_4 (*c*) MCl_3 (*d*) MCl

22. An organic compound gives 0.220 g of CO_2 and 0.126 g of H_2O on complete combustion. If the % of carbon is 24, then the % hydrogen is ________ $\times 10^{-1}$. (Nearest integer) **[13 April, 2023 (Shift-I)]**

23. 116 g of a substance upon dissociation reaction yields 7.5 g of hydrogen, 60g of oxygen and 48.5 g of carbon. Given that the atomic masses of H, O and C are 1,16 and 12 g/mol respectively. The data agrees with how many formulae of the following? **[27 June, 2022 (Shift-II)]**

(*a*) CH_3COOH (*b*) HCHO

(*c*) CH_3OOCH_3 (*d*) CH_3CHO

24. A 2.0 g sample containing MnO_2 is treated with HCl liberating Cl_2. The Cl_2 gas is passed into a solution of KI and 60.0 mL of 0.1 M $Na_2S_2O_3$ is required to titrate the liberated iodine. The percentage of MnO_2 in the sample is____. (Nearest integer)

[Atomic masses (in u) Mn = 55; Cl = 35.5; O = 16, I = 127, Na = 23, K = 39, S = 32] **[28 June, 2022 (Shift-I)]**

25. Complete combustion of 750g of an organic compound provides 420 g of CO_2 and 210 g of H_2O. The percentage composition of carbon and hydrogen in organic compound is 15.3 and ________ respectively. (Round off to the nearest Integer). **[16 March, 2021 (Shift-I)]**

26. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 ml of CO_2 at T = 298.15 K and p = 1 bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet? [Molar mass of $NaHCO_3$ = 84 g mol^{-1}] **[11 Jan, 2019 (Shift-I)]**

(*a*) 0.84 (*b*) 33.6 (*c*) 16.8 (*d*) 8.4

STOICHIOMETRY & STOICHIOMETRIC CALCULATIONS

27. Mass of methane required to produce 22 g of CO_2 after complete combustion is ______ g.

(Given Molar mass in g mol^{-1}

C = 12.0

H = 1.0

O = 16.0) **[27 Jan, 2024 (Shift-I)]**

28. Number of moles of methane required to produce 22g $CO_{2(g)}$ after combustion is x × 10^{-2} moles. The value of x is **[31 Jan, 2024 (Shift-I)]**

29. Consider the following reaction:

$3PbCl_2 + 2(NH_4)_3PO_4 \rightarrow Pb_3(PO_4)_2 + 6NH_4Cl$

If 72 mmol of $PbCl_2$ is mixed with 50 mmol of $(NH_4)_3PO_4$, then amount of $Pb_3(PO_4)_2$ formed is ______ mmol. (nearest integer) **[01 Feb, 2024 (Shift-I)]**

30. Combustion of glucose ($C_6H_{12}O_6$) produces CO_2 and water. The amount of oxygen (in g) required for the complete combustion of 900 g of glucose is: (Molar mass of glucose in $gmol^{-1}$) = 180 **[08 April, 2024 (Shift-I)]**

(*a*) 480 (*b*) 960 (*c*) 800 (*d*) 32

31. The number of moles of methane required to produce 11g CO_2(g) after complete combustion is:

(Given molar mass of methane in g mol^{-1} : 16) **[05 April, 2024 (Shift-II)]**

(*a*) 0.75 (*b*) 0.25 (*c*) 0.35 (*d*) 0.5

32. 1 g of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01 mol of CO_2. The molar mass of M_2CO_3 is ___ g mol^{-1}. (Nearest integer) **[13 April, 2023 (Shift-II)]**

33. If a rocket runs on a fuel ($C_{15}H_{30}$) and liquid oxygen, the weight of oxygen required and CO_2 released for every litre of fuel respectively are: **[24 June, 2022 (Shift-I)]**

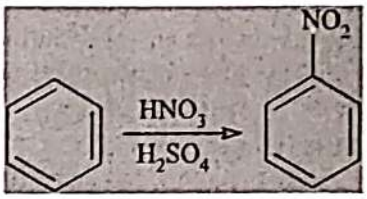
(Given: density of the fuel is 0.756 g / mL)

(*a*) 1188 g and 1296 g (*b*) 2376 g and 2592 g

(*c*) 2592 g and 2376 g (*d*) 3429 g and 3142 g

34. A 0.166 g sample of an organic compound was digested with conc. H_2SO_4 and then distilled with NaOH. The ammonia gas evolved was passed through 50.0 mL of 0.5 N H_2SO_4. The used acid required 30.0 mL of 0.25 N NaOH for complete neutralization. The mass percentage of nitrogen in the organic compound is__________. **[24 June, 2022 (Shift-I)]**

35.



In the above reaction, 3.9 g of benzene on nitration gives 4.92 g of nitrobenzene. The percentage yield of nitrobenzene in the above reaction is____________%

(Round off to the nearest integer).

(Given atomic mass : C : 12.0 u, H : 1.0 u, O : 16.0 u, N : 14.0 u) **[17 March, 2021 (Shift-I)]**

36. For a reaction,

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$;

Identify dihydrogen (H_2) as a limiting reagent in the following reaction mixtures. **[9 April, 2019 (Shift-I)]**

(*a*) 14 g of N_2 + 4 g of H_2 (*b*) 28 g of N_2 + 6 g of H_2

(*c*) 56 g of N_2 + 10 g of H_2 (*d*) 35 g of N_2 + 8 g of H_2

PW Challengers

NUMERICAL TYPE QUESTIONS (ANSWER UPTO TWO DECIMAL PLACE)

1. Excess of calcium orthophosphate is reacted with magnesium to from Ca_3P_2 along with MgO. Ca_3P_2 on reaction with water liberated PH_3 along with $Ca(OH)_2$. PH_3 is burnt in excess of oxygen to form P_2O_5 along with water. Oxides of magnesium and phosphorous react to give magnesium metaphosphate. Calculate grams of magnesium metaphosphate obtained if 1.92 gm of Mg is taken (Mg = 24, P = 31, O = 16)

2. In one process for waterproofing, a fabric is exposed to $(CH_3)_2SiCl_2$ vapour. The vapour reacts with hydroxyl groups on the surface of the fabric or with traces of water to form the waterproofing film $[(CH_3)_2SiO]_n$, by the reaction

   $$n[(CH_3)_2SiCl_2 + 2nOH^- \rightarrow 2nCl^- + nH_2O + [(CH_3)_2SiO]_n$$

   Where n stands for a large integer. The waterproofing film is deposited on the fabric layer upon layer. Each layer is 6.0 Å thick [the thickness of the $(CH_3)_2SiO$ group]. How much (in g) $(CH_3)_2$ $SiCl_2$ is needed to waterproof one side of a piece of fabric, 1.00 m by 3.70 m, with a film 300 layers thick ? The density of the film is 1.0 g/cm^3. (Si = 28)

   Molar mass of $(CH_3)_2SiO$ = 74 g/mol

   Molar mass of $(CH_3)_2SiCl_2$ = 129 g/mol

INTEGER TYPE QUESTIONS

3. Cis-platin $[Pt(NH_3)_2Cl_2]$, a compound used in cancer treatment is prepared by the reaction of ammonia with potassium tetrachloroplatinate.

   $$K_2PtCl_4 + 2NH_3 \rightarrow 2KCl + Pt(NH_3)_2Cl_2$$

   (i) How many grams of cis-platin are formed from 41.5 gm K_2PtCl_4 amd 34 gm NH_3, if the reaction takes place in 90% yield? (Ans. x)

   (ii) What is the maximum mass (in gm) of KCl which can be produced if initially total 9 moles of reactant are taken. Assuming 100% reaction ? (Ans. y)

   What is the value of (x + y)? [Pt = 195, K = 39, Cl = 35.5]

4. The number of Alkoxy groups in an organic compound $A(OR)_x$ may be determined by the sequential reaction.

   $$A(OR)_x + xHI \rightarrow A(OH)_x + xRI$$

   $$RI + Ag^+ + H_2O \rightarrow ROH + AgI(s) + H^+$$

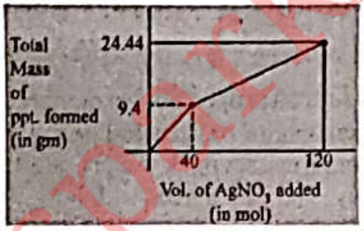
   When 4.8 gm of organic compound $A(OR)_x$ (molar mass = 240 gm mol^{-1}) is treated as above, 9.4 gm AgI is precipitated. Then, calculate number of alkoxy groups in the compound $A(OR)_x$? (I = 127, Ag = 108)

5. A sample of ammonia contains only H^1 and H^2 isotopes of hydrogen in 4:1 ratio and N^{14} and N^{15} isotopes of nitrogen in 3:1 ratio. How many neutrons are present in 1.785 mg of ammonia? (Answer in the order of 10^{18})($N_A = 6 \times 10^{23}$)

6. In order to determine the composition of a mixture of halides containing MBr_2 & NaI, 14 gm mixture was dissolved in water. To this solution, $AgNO_3$ solution of certain molarity was added gradually. The mass of precipitate produced (in gm) were measured and it was plotted against volume of $AgNO_3$ solution added (in ml). If it is known that AgI is precipitated first and precipitation of Br^- does not start until the already precipitating I^- precipitates completely. Find out the value of AB × CD where:

   AB = Atomic weight of metal 'M'

   CD = Mole percent of NaI in original mixture.



   (Molar mass of NaI = 149.89g/mol, Br = 79.9g/mol, AgI = 234.77g/mol)

7. A mixture of gases liberated upon decomposition of 33.1 gm $Pb(NO_3)_2$ is dissolved in 10ml of water. What is the mass (in g) of 0.1M KOH solution with density 1.05 g/ml required to neutralise this acid. The reactions involved are: (at. mass of Pb = 207)

   $$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

   $$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

   $$KOH + HNO_3 \rightarrow KNO_3 + H_2O$$

8. Water is the working Fluid in a thermal plant for producing electricity. Coal is Combusted for Generating heat as per reaction, $C + O_2 \rightarrow CO_2$. 0.01% of the released CO_2 gas is absorbed in water and gets converted into weak acid, H_2CO_3 which dissociate to give H^+ as $H_2CO_3 \rightarrow 2H^+ + CO_3^{-2}$. The % dissociation of acid is 5%. Assume no ionisation of H_2O. If in a certain application $[H^+]$ concentration can maximum be 10^{-5} M, then

   (a) Calculate maximum no. of moles of H^+(x) and CO_3^{-2} (y) in water if 10^9 litres of H_2O is used.

   (b) Calculate maximum no. of mole of carbon (z) which can be burnt so that water remains fit to be used.

   What is the value of xy^2/z?

9. A mother cell disintegrates into 60 identical cells and each daughter cell of mother disintegrates into 24 smaller cells, The smallest cell is uniform cylindrical in shape with diameter 120Å and each cell is 6000Å long. Determine molar mass of the mother cell, if density of the smallest cell is 1.12 gm/cm^3. Using scientific notation if your answer is x × 10^y, their write the value of [x] + y, where [ ] is an integer function. Take avogadro number as 6×10^{23}.

10. Once Tom & Jerry entered a chemistry lab where a chemist was preparing 3L H_2SO_4 solution. He labelled the solution as 10 m ($d_{solution} = 3.3$ gm/ml). As the chemist left the lab, a mischief came in Tom's mind. He tried to throw the solution on Jerry but failed. In doing so some of the H_2SO_4 solution fell on the floor, so he added water to make it again to 3L. The chemist returned back & got astonished when he saw the result of analysis, that were d = 1.5 gm/ml and % w/w = 98. Find out the number of moles of H_2SO_4 which fell down on the floor.

11. A polymeric substance, tetrafluoroethylene, can be represented by the formula $(C_2F_4)_x$, where x is a large number. The material was prepared by polymerizing C_2F_4 in the presence of a sulphur bearing catalyst that serves as a nucleus upon which the polymer grew. The final product was found to contain 0.012% S. What is the value of x, if each polymeric molecule contains one sulphur atom? Assume that the catalyst contributes a negligible amount to the total mass of the polymer. (F = 19, S = 32)

SINGLE CHOICE TYPE QUESTIONS

12. Density of water varies with temperature as shown.

$d_{t°C} = d_{0°C} - (0.002 \times t°C)$; where

$d_{t°C}$ = density at t°C and $d_{0°C}$ = density at 0°C = 1gm/ml

Calculate % change in molarity and molality respectively of pure water due to change in temperature from 0°C to 100°C.

(*a*) 10%, no change

(*b*) no change, 20%

(*c*) 20%, no change

(*d*) 20%, 20%

> *"You may have to fight a battle more than once to win it."*
> *– Margaret Thatcher*

ANSWER KEY

CONCEPT APPLICATION

1. (*a*) **2.** (*a*) **3.** (*d*) **4.** (*a*) **5.** (*a*) **6.** (*a*) **7.** (*a*) **8.** (*b*) **9.** (*b*) **10.** (*b*)
11. (*a*) **12.** (*b*) **13.** (*c*) **14.** (*b*) **15.** (*a*) **16.** (*b*) **17.** (*b*) **18.** (*a*) **19.** (*c*) **20.** (*d*)
21. (*d*) **22.** (*b*) **23.** (*a*) **24.** (*c*) **25.** (*b*) **26.** (*c*) **27.** (*c*) **28.** (*b*) **29.** (*c*) **30.** (*d*)
31. (*a*) **32.** (*b*)

SCHOOL LEVEL PROBLEMS

1. (*b*) **2.** (*a*) **3.** (*a*) **4.** (*b*) **5.** (*c*) **6.** (*a*) **7.** (*a*) **8.** (*b*) **9.** (*c*) **10.** (*a*)
11. (i)-(*r*), (ii)-(*s*), (iii)-(*q*), (iv)-(*p*) **12.** (i)-(*q*), (ii)-(*r*), (iii)-(*p*), (iv)-(*t*), (v)-(*s*) **24.** I-(*b*), II-(*b*), III-(*a*), IV-(*a*)

PRARAMBH (TOPICWISE)

1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*a*) **8.** (*b*) **9.** (*a*) **10.** (*d*)
11. (*a*) **12.** (*a*) **13.** (*a*) **14.** (*b*) **15.** (*b*) **16.** (*a*) **17.** (*a*) **18.** (*c*) **19.** (*c*) **20.** (*d*)
21. (*b*) **22.** (*a*) **23.** (*a*) **24.** (*d*) **25.** (*c*) **26.** (*b*) **27.** (*b*) **28.** (*c*) **29.** (*c*) **30.** (*c*)
31. (*c*) **32.** (*a*) **33.** (*a*) **34.** (*a*) **35.** (*d*) **36.** (*a*) **37.** (*c*) **38.** (*d*) **39.** (*b*) **40.** (*c*)
41. (*a*) **42.** (*d*) **43.** (*d*) **44.** (*d*) **45.** (*a*)

PRABAL (JEE MAIN LEVEL)

1. (*c*) **2.** (*a*) **3.** (*c*) **4.** (*a*) **5.** (*c*) **6.** (*b*) **7.** (*a*) **8.** (*a*) **9.** (*a*) **10.** (*d*)
11. (*c*) **12.** (*a*) **13.** (*a*) **14.** (*b*) **15.** (*a*) **16.** (*b*) **17.** (*b*) **18.** (*a*) **19.** (*a*) **20.** (*a*)
21. (*a*) **22.** (*a*) **23.** (*d*) **24.** (*b*) **25.** (*c*) **26.** (*b*) **27.** (*b*) **28.** (*c*) **29.** (*b*) **30.** (*b*)
31. (*c*) **32.** (*b*) **33.** (*c*) **34.** (*a*) **35.** (*c*) **36.** (*c*) **37.** (*c*) **38.** (*a*) **39.** (*a*) **40.** (*b*)
41. (*c*) **42.** (*c*) **43.** (*a*) **44.** (*d*) **45.** (*c*) **46.** (*a*) **47.** [300] **48.** [76] **49.** [83] **50.** [207]
51. [4] **52.** [80] **53.** [30M, 75m] **54.** [2] **55.** [180]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*c*) **2.** (*d*) **3.** (*a*) **4.** (*c*) **5.** (*b*) **6.** (*c*) **7.** (*a*) **8.** (*d*) **9.** (*b*) **10.** (*a*)
11. (*c*) **12.** (*b*) **13.** (*a*) **14.** (*a*) **15.** (*b*) **16.** (*c*) **17.** (*b*) **18.** (*a*) **19.** (*c*) **20.** (*a,b,c*)
21. (*b,c,d*) **22.** (*a,b,c*) **23.** (*a,c*) **24.** (*b,d*) **25.** (*b,d*) **26.** (*a,b*) **27.** (*a,b,d*) **28.** (*a,b,d*) **29.** (*a,b,c*) **30.** (*a,c*)
31. (*a,c,d*) **32.** (*a,b,d*) **33.** (*a,b*) **34.** (*b,c,d*) **35.** (*a*) **36.** (*b*) **37.** (*b*) **38.** (*b*) **39.** (*c*) **40.** (*b*)
41. (*c*) **42.** (*b*) **43.** (*b*) **44.** (*b*) **45.** (*d*) **46.** [1811.5] **47.** [0.29] **48.** [73.6] **49.** [3]
50. [28] **51.** [3] **52.** [75] **53.** [50] **54.** [2400] **55.** [32]

PYQ's (PAST YEAR QUESTIONS)

1. (*b*) **2.** (*c*) **3.** (*b*) **4.** [8] **5.** (*b, c*) **6.** (*a*) **7.** (*d*) **8.** (*b*) **9.** [11] **10.** (*d*)
11. [200] **12.** (*c*) **13.** [1] **14.** [2130] **15.** (*c*) **16.** [6.15] **17.** (*a*) **18.** [14] **19.** (*d*) **20.** (*a*)
21. (*a*) **22.** [56] **23.** (*b*) **24.** [13] **25.** [3] **26.** (*d*) **27.** [8] **28.** [50] **29.** [24] **30.** (*b*)
31. (*b*) **32.** [100] **33.** (*c*) **34.** [63] **35.** [80] **36.** (*c*)

PW CHALLENGERS

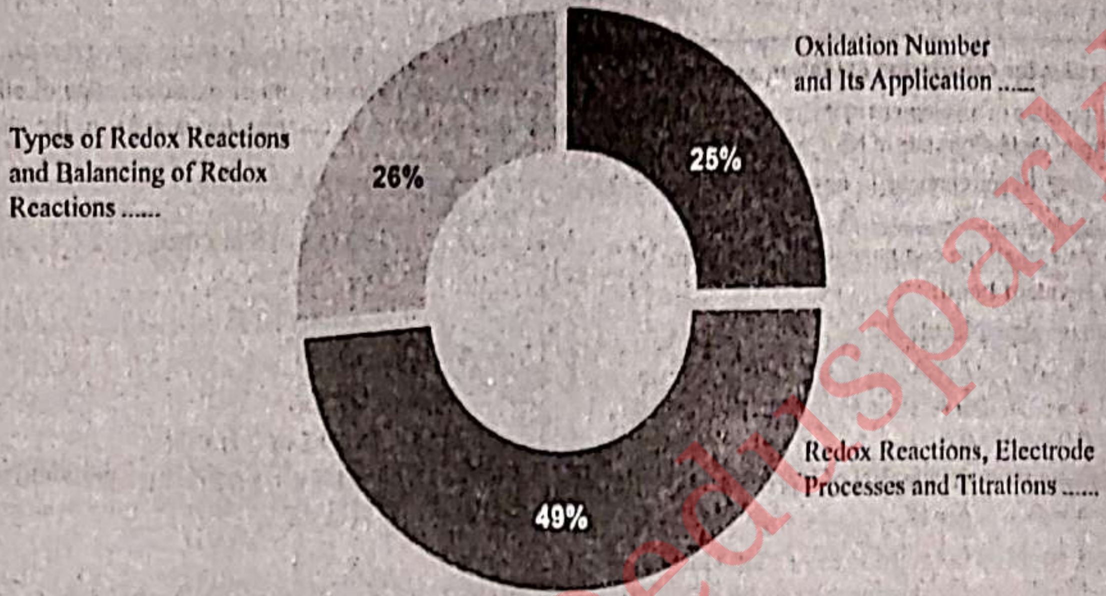
1. [1.82] **2.** [1.16] **3.** [474] **4.** [2] **5.** [471] **6.** [4994] **7.** [2100] **8.** [250] **9.** [16] **10.** [5]
11. [2667] **12.** (*c*)

CHAPTER

3

Redox Reaction

Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

INTRODUCTION

Redox reactions shows vital role in non renewable energy sources. In cell reactions where oxidation and reduction both occurs simultaneously will have redox reaction for interconversion of energy.

REDOX REACTION IN TERM OF ELECTRON TRANSFER REACTIONS (MODERN IDEA)

Oxidation

- De-electronation
- Oxidation process is those process in which one or more e^- are lost by an atom, ion or molecule.

  Example: $Zn \rightarrow Zn^{+2} + 2e^-$

  $M \rightarrow M^{n+} + ne^-$

Reduction

- Electronation
- Reduction process is those process in which one or more e^- are gained by an atom, ion or molecule.

  Example: $Cu^{+2} + 2e^- \rightarrow Cu$

  $M^{n+} + ne^- \rightarrow M$

Redox Reaction (Oxidation-Reduction): Many chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as **oxidation-reduction** or **redox reactions.**

or

Those reactions which involve oxidation and reduction both simultaneously are known as oxidation reduction or redox reactions.

or

Those reactions in which increase as well as decrease in oxidation number of same or different atoms occurs are known as redox reactions.

Oxidation State: Oxidation state of an atom in a molecule or ion is the hypothetical or real charge present on an atom due to electronegativity difference.

or

Oxidation state of an element in a compound represents the number of electrons lost or gained during its change from free elemental state into that compound.

Some important points concerning oxidation number

1. Oxidation number of an element may be positive or negative.
2. Oxidation number may be zero, whole number or a fractional value

Ex. $Ni(CO)_4 \Rightarrow$ O.S of Ni = 0
$N_3H \Rightarrow$ O.S of N = −1/3
$HCl \Rightarrow$ O.S of Cl = −1

3. Oxidation state of same element can be different in same or different compounds.

Ex. $H_2S \Rightarrow$ O.S of S = −2
$H_2SO_3 \Rightarrow$ O.S of S = +4
$H_2SO_4 \Rightarrow$ O.S of S = +6

❖ **Electronegativity:** P > H   C > H   S > C   Cl > N

Some helping rules for calculating oxidation number:

- ❖ The oxidation state of an element in its free (elemental) state is zero. Example: Oxidation state of Na, Cu, I, Cl, O etc., are zero.
- ❖ Oxidation state of an element in any of its allotropic form (eg. $C_{Diamond}$, $C_{Graphite}$, $S_{Monoclinic}$, $S_{Rhombic}$) is zero.
- ❖ Oxidation state of all the components of an alloy are 0

(A) In case of covalent bond:

(*i*) For homoatomic molecule

$$\begin{array}{ccc} A-A & A=A & A\equiv A \\ \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow \\ 0\ 0 & 0\ 0 & 0\ 0 \end{array}$$

(*ii*) For heteroatomic molecule (EN of B>A)

$$\begin{array}{ccc} A-B & A=B & A\equiv B \\ \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow \\ +1\ -1 & +2\ -2 & +3\ -3 \end{array}$$

(*iii*) Oxidation state of atoms present in homoatomic molecules is zero

Ex. H_2, O_2, N_2, P_4, S_8 = zero

(*iv*) In complex compounds, oxidation state of some neutral molecules (ligands) is zero. Example CO, NO, NH_3, H_2O

(*v*) Oxidation state of fluorine in all its compounds is −1

(*vi*) Oxidation state of group 1 & 2 elements are +1 and +2 respectively in their compounds.

(*vii*) Oxidation state of hydrogen in most of its compounds is +1 except in metal hydrides (−1)

$$\begin{array}{lcccc} \textbf{Ex.} & NaH & LiH & CaH_2 & MgH_2 \\ & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow & \downarrow\downarrow \\ & +1\ -1 & +1\ -1 & +2\ -1 & +2\ -1 \end{array}$$

(*viii*) Oxidation state of oxygen in most of its compounds is −2 except in:

(*a*) Peroxides $\left(O_2^{2-}\right) \rightarrow$ Oxidation state (O) = −1

Ex. H_2O_2, BaO_2

(*b*) Super Oxides $\left(O_2^{1-}\right) \rightarrow$ Oxidation state (O) = −1/2

Ex. KO_2

(*c*) Ozonide $\left(O_3^{1-}\right) \rightarrow$ Oxidation state (O) = −1/3

Ex. KO_3

(*d*) OF_2(Oxygen difluoride) Oxidation state (O) = +2

F–O–F

(*e*) O_2F_2 (dioxygen difluoride) Oxidation state (O) = +1

(*ix*) The algebric sum of oxidation state of all the atoms present in a polyatomic neutral molecule is 0.

Ex. H_2SO_4
If O.S of S is x then
$2(+1) + x + 4(-2) = 0$
$x - 6 = 0$
$x = +6$

Ex. H_2SO_3
If O.S of S is x then
$2(+1) + x + 3(-2) = 0$
$x - 4 = 0$
$x = +4$

(*x*) The algebraic sum of oxidation state of all the atoms in a polyatomic complex ion is equal to the charge present on the ion.

Ex. SO_4^{2-}
If O.S of S is x then
$x + 4(-2) = -2$
$x - 8 = -2$
$x = +6$

Ex. $H\underline{C}O_3^-$
If O.S of C is x then
$+1 + x + 3(-2) = -1$
$x - 5 = -1$
$x = +4$

(B) In case of co-ordinate bond (EN of B>A):

$$\begin{array}{cc} A\rightarrow B & B\rightarrow A \\ \downarrow\ \ \downarrow & \downarrow\ \ \downarrow \\ +2\ -2 & \text{(neglected)} \end{array}$$

(C) In case of Ionic bond:

Oxidation state of monoatomic ions is equal to the charge present on the ion.

Ex. $Mg^{2+} \rightarrow$ Oxidation state = +2

e.g., Charge on cation = O.S of cation
Charge on anion = O.S of anion

$$\begin{array}{llcccc} \textbf{Ex:} & NaCl & \rightarrow & Na^+ & + & Cl^- \\ & & & \downarrow & & \downarrow \\ & & & +1 & & -1 \\ & MgCl_2 & \rightarrow & Mg^{2+} & + & 2Cl^- \\ & & & \downarrow & & \downarrow \\ & & & +2 & & -1 \end{array}$$

OXIDISING AND REDUCING AGENT

❖ **Oxidising agent or Oxidant:** Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants.

e.g. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc.H_2SO_4 etc. are powerful oxidising agents.

- **Reducing agent or Reductant:** Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

  e.g. KI, $Na_2S_2O_3$ etc. are the powerful reducing agents.

TYPES OF REDOX REACTION

Type of Redox Reaction

(*i*) Intermolecular redox reaction

(*ii*) Intramolecular redox reaction

(*iii*) Disproportionation reaction

(*iv*) Comproportionation reaction

(*i*) **Intermolecular redox reaction:** A redox reaction in which oxidising agent and reducing agent are two different compounds.

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow$

$5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

It is intermolecular redox reaction.

(*ii*) **Disproportionation Reaction:** A redox reaction in which same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.

Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states**. The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction. For example:

$$2H_2\overset{-1}{O_2}(aq) \rightarrow 2H_2\overset{-2}{O}(\ell) + \overset{0}{O_2}(g)$$

$$\overset{0}{S_8}(s) + 12OH^-(aq) \rightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(\ell)$$

$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \rightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl^-}(aq) + H_2O(\ell)$$

$$4K\overset{+5}{Cl}O_3 \rightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$$

(*iii*) **Intra molecular redox reaction:**

Here both elements undergoing oxidation & reduction belongs to same compound.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

$KClO_3$ plays a role of oxidant and reductant both. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. Since same element is not oxidized and reduced, so **it is not a disproportionation reaction,** although it looks like one.

It is called intra molecular redox reaction.

(*iv*) **Comproportionation reaction:**

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Nitrogen in this compound has –3 and +3 oxidation number, which is not a definite value. So it is not a disproportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state. Comproportionation reactions are reverse reactions of disproportionation reactions.

BALANCING OF REDOX REACTIONS

Balancing of Redox Equation

(*a*) Ion electron method.

(*b*) Oxidation number change method.

(*a*) **Ion electron method:**

The following steps are followed while balancing redox reaction (equations) by this method.

(*i*) Write the equation in ionic form.

(*ii*) Split the redox equation into two half reactions, one representing oxidation and the other representing reduction.

(*iii*) Balance these half reactions separately for atoms other than 'O' and 'H'.

(*iv*) Then balance oxygen atoms by adding H_2O molecules to the side deficient in oxygen. The number of H_2O molecules added is equal to the number of deficiency of oxygen atoms.

(*v*) Balance hydrogen atoms by adding H^+ ions equal to the deficiency on the side which is deficient in hydrogen atoms.

(*vi*) Finally if the medium of reaction is basic, OH^- ions are added to both sides of balanced equation equal in number of H^+ in balanced equation.

(*vii*) Balance the charge by adding electrons to the side which is rich in +ve charges. i.e. deficient in electrons. Number of electrons added is equal to the deficiency.

(*viii*) Multiply the half equations with suitable coefficients to equalize the number of electrons.

(*ix*) Add these half equations to get an equation which is balanced with respect to charge and atoms.

(*b*) **Oxidation number change method:** In a balanced redox reaction, total increase in oxidation number must be equal to total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions.

The general procedure involves the following steps:

(*i*) Select the atom in oxidising agent whose oxidation number decreases and indicate the number of gain of electrons per molecule.

(*ii*) Select the atom in reducing agent whose oxidation number increases and find the number of loss of electrons per molecule.

(*iii*) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.

(*iv*) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.

(*v*) In order to balance oxygen atoms, add required number of H_2O molecules to the side deficient in oxygen. Then balance the required number of H atoms by adding H^+ ions to the side deficient in the hydrogen.

Train Your Brain

Example 1: Balance the following redox reaction by ion electron method:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Sol. **Step-I:** Assign the oxidation number to each element present in the reaction.

$$\overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \rightarrow \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

Step-II: Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

Step-III: Now identify the oxidation/reduction occurring in the reaction

undergoes reduction

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

undergoes oxidation

Step-IV: Spilt the Ionic reaction in two half reactions, one for oxidation and other for reduction.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \,\Big|\, MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

Step-V: Balance the atom other than oxygen and hydrogen atom in both half reactions

$$Fe^{2+} \longrightarrow Fe^{3+} \,\Big|\, MnO_4^- \longrightarrow Mn^{2+}$$

Fe & Mn atoms are balanced on both side.

Step-VI: Now balance O & H atom by H_2O & H^+ respectively by the following way: For one excess oxygen atom, add one H_2O on the other side and two H^+ on the same side.

$Fe^{2+} \longrightarrow Fe^{3+}$ (no oxygen atom) ...(*i*)

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ...(*ii*)

Step-VII: Equation (*i*) & (*ii*) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ...(*i*)

$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O$ ...(*ii*)

Step-VIII: The number of electrons gained and lost in each half-reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

Here, we multiply equation (*i*) by 5 and (*ii*) by 1 and add them:

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ ....(*i*) × 5

$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ ....(*ii*)×1

$5Fe^{2+} + 8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

(Here, at this stage, you will get balanced redox reaction in Ionic form)

Step-IX: Now convert the Ionic reaction into molecular form by adding the elements or species, which are removed in step (2).

Now, by some manipulation, you will get:

$$5\,FeSO_4 + KMnO_4 + 4H_2SO_4 \longrightarrow \frac{5}{2}\,Fe_2(SO_4)_3 + MnSO_4 + 4H_2O + \frac{1}{2}\,K_2SO_4$$

or

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4.$$

Example 2: Balance the following redox reaction in basic medium by ion electron method.

$$ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$$

Sol. By using upto step V, we will get:

$$\overset{+1}{Cl}O^- \xrightarrow{\text{Reduction}} Cl^-;\ \overset{+3}{Cr}O_2^- \xrightarrow{\text{Oxidation}} \overset{+6}{Cr}O_4^{2-}$$

Now, students are advised to follow step VI to balance 'O' and 'H' atom.

$2H^+ + ClO^- \rightarrow Cl^- + H_2O$

$2H_2O + CrO_2^- \rightarrow CrO_4^{2-} + 4H^+$

Now, since we are balancing in basic medium, therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.

$2OH^- + 2H^+ + ClO^- \longrightarrow Cl^- + H_2O + 2OH^-$,

$4OH^- + 2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+ + 4OH^-$

Finally you will get

$H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ...(*i*)

$4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O$ ...(*ii*)

Now from step VIII

$2e^- + H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ...(*i*) ×3

$4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^-$ ...(*ii*) ×2

Adding:

$3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

Example 3: Balance the following reaction by the oxidation number method:

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Sol. Write the oxidation number of all the atoms.

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

There is change in oxidation number of Cu and N.

$\overset{0}{Cu} \longrightarrow \overset{2+5-2}{Cu(NO_3)_2}$ ....(*i*) (Oxidation number of Cu is increased by 2)

$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2}$ ....(*ii*) (Oxidation number of N is decreased by 1)

To make increase and decrease equal, eq. (*ii*) is multiplied by 2.

$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$

Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

This is the balanced equation.

Concept Application

1. The oxidation numbers of C in HCN and HNC, respectively, are
   (*a*) +2, +2 (*b*) +2, +4
   (*c*) +4, +4 (*d*) −2, −2
2. What is the oxidation state of Xe in Ba_2XeO_6?
   (*a*) 0 (*b*) +4 (*c*) +6 (*d*) +8
3. When $K_2Cr_2O_7$ is converted into K_2CrO_4, the change in oxidation number of Cr is
   (*a*) 0 (*b*) 6 (*c*) 4 (*d*) 3
4. In the reaction: $3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$
   (*a*) Bromine is oxidized and carbonate is reduced.
   (*b*) Bromine is oxidized and water is reduced.
   (*c*) Bromine is both oxidized and reduced.
   (*d*) Bromine is neither oxidized nor reduced.
5. Which of the following reaction is not a disproportionation reaction?
   (*a*) $Br_2 + CO_3^{2-} + H_2O \rightarrow Br^- + BrO_3^- + HCO_3^-$
   (*b*) $P_4 + OH^- + H_2O \rightarrow PH_3 + H_2PO_2^-$
   (*c*) $H_2S + SO_2 \rightarrow S + H_2O$
   (*d*) $H_2O_2 \rightarrow H_2O + O_2$
6. For the redox reaction,
   $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$
   in basic medium, the coefficients of Zn, NO_3^- and OH^- in the balanced equation, respectively, are:
   (*a*) 4, 1, 7 (*b*) 7, 4, 1
   (*c*) 4, 1, 10 (*d*) 1, 4, 10

TYPES OF REDOX REACTIONS

1. Combination reactions

A combination reaction may be denoted in the manner:

$$A + B \rightarrow C$$

Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions.

e.g., $\overset{0}{C}(s) + \overset{0}{O}_2(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O}_2(g)$

2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state.

e.g., $2\overset{+1}{H}_2\overset{-2}{O}(l) \xrightarrow{\Delta} 2\overset{0}{H}_2(g) + \overset{0}{O}_2(g)$

All decomposition reactions are not redox reactions.
e.g., $\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O}_3(s) \xrightarrow{\Delta} \overset{+2}{Ca}\overset{-2}{O}(s) + \overset{+4}{C}\overset{-2}{O}_2(g)$

3. Displacement reactions

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element.

$$X + YZ \rightarrow XZ + Y$$

(a) **Metal displacement:** A metal in a compound can be displaced by another metal in the uncombined state.

e.g., $\overset{+2}{Cu}\overset{+6}{S}\overset{-2}{O}_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O}_4(aq)$

(b) **Non-metal displacement:** The non-metal displacement redox reactions include hydrogen displacement and a rarely occutring reaction involving oxygen displacement.

e.g., $2\overset{0}{Na}(s) + 2\overset{+1}{H}_2\overset{-2}{O}(\ell) \rightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H}_2(g)$

$2\overset{+1}{H}_2\overset{-2}{O}(\ell) + 2\overset{0}{H}_2O(g) \rightarrow 4\overset{+1}{H}\overset{-1}{F}(aq) + \overset{0}{O}_2(g)$

APPLICATIONS OF OXIDATION NUMBER

(*a*) **To compare the strength of oxyacid:**

Strength of oxyacid ∝ Oxidation Number

Example: Order of acidic strength in HClO, $HClO_2$, $HClO_3$, $HClO_4$ will be

Sol. Oxidation Number of chlorine

HClO (Hypo chlorous acid)	+1
$HClO_2$ (Chlorous acid)	+3
$HClO_3$ (Chloric acid)	+5
$HClO_4$ (Perchloric acid)	+7

∵ Strength of oxyacid ∝ Oxidation Number

So the acidic strength order will be:

$HClO_4 > HClO_3 > HClO_2 > HClO$

(*b*) **To determine the oxidising and reducing nature of the substances:**

Highest O.S.	+4	+5	+5	+6	+7	+6	+7	+8	+8	+2	+1
Elements	C	N	P	S	Cl	Cr	Mn	Os	Ru	O	H
Lowest O.S.	−4	−3	−3	−2	−1	0	0	0	0	−2	−1

(*i*) If effective element in a compound is present in maximum oxidation state then the compound acts as oxidising agent.

Example:

$KMnO_4$	$K_2Cr_2O_7$	H_2SO_4	SO_3	H_3PO_4	HNO_3	$HClO_4$
↓	↓	↓	↓	↓	↓	↓
+7	+6	+6	+6	+5	+5	+7

(*ii*) If effective element in a compound is present in minimum oxidation state then the compound acts as reducing agent.

PH_3	NH_3	CH_4
↓	↓	↓
−3	−3	−4

(*iii*) If effective element in a compound is present in intermediate oxidation state then the compound can act as oxidising agent as well as reducing agent.

HNO_2	H_3PO_3	SO_2	H_2O_2
↓	↓	↓	↓
+3	+3	+4	−1

Key Note

- ❖ Max. O.S. = No of valence e^- } (for an element)
- ❖ Min. O.S. = 8 – (no. of valence e^-) }

(c) To calculate the equivalent weight of compounds: The equivalent weight of an oxidising agent or reducing agent is that weight which accepts one mole electrons in a chemical reaction or loses one mol electron in chemical reaction.

(*i*) Equivalent weight of oxidant

$$= \frac{\text{Molecular weight}}{\text{No.of electrons gained by one molecule}}$$

$$= \frac{M}{\text{Total change in O.N. per molecule}}$$

Example: In acidic medium

$6e^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Here atoms which undergoes reduction is Cr. Its O.S. is decreasing from +6 to +3

Equivalent weight of $K_2Cr_2O_7$

$$= \frac{\text{Molecular weight of } K_2Cr_2O_7}{3 \times 2} = \frac{M}{6}$$

(*ii*) Equivalent weight of a reducant

$$= \frac{\text{Molecular weight}}{\text{No.of electrons lost by one molecule}}$$

$$= \frac{M}{\text{Total change in O.N. per molecule}}$$

In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

Equivalent weight of $C_2O_4^{2-} = \frac{M}{2}$

(*iii*) In different conditions a compound may have differen equivalent wts. Because, it depends upon the number o electrons gained or lost by that compound in that reaction

(*d*) **To determine the possible molecular formula of compound** Since the sum of oxidation number of all the atoms presen in a compound is zero, so the validity of the formula can b confirmed.

Table: Some important oxidising & reducing agents.

Species	Changed to	Reaction	No. of electrons exchanged or change in O.N.	Eq. wt.
MnO_4^- (O.A.)	Mn^{+2} In acidic medium	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	5	$E = \frac{M}{5}$
MnO_4^- (O.A.)	MnO_2 In neutral medium or weak alkaline medium	$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$	3	$E = \frac{M}{3}$
MnO_4^- (O.A.)	MnO_4^{2-} Strongly basic medium	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	1	$E = \frac{M}{1}$
$Cr_2O_7^{2-}$ (O.A.)	Cr^{3+} In acidic medium	$CrO_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	6	$E = \frac{M}{6}$
MnO_2 (O.A.)	Mn^{2+} In acidic medium	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	2	$E = \frac{M}{2}$
Cl_2 (O.A.)	Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	2	$E = \frac{M}{2}$
$CuSO_4$ (O.A.) in iodometric titration	Cu^+	$Cu^{2+} + e^- \rightarrow Cu^+$	1	$E = \frac{M}{1}$
$S_2O_3^{2-}$ (R.A.) (Hypo)	$S_4O_6^{2-}$	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$	2 (for two molecules)	$E = \frac{2M}{2} = M$
H_2O_2 (O.A.)	H_2O	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	2	$E = \frac{M}{2}$
H_2O_2 (R.A.)	O_2	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ O.N. of oxygen in H_2O is –1 per atom	2	$E = \frac{M}{2}$
Fe^{2+} (R.A.)	Fe^{3+}	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	1	$E = \frac{M}{1}$

Table: Some important oxidising & reducing agents.

Species	Changed to	Reaction	No. of electrons exchanged or change in O.N.	Eq. wt.
$C_2O_4^{2-}$ (RA)	CO_2	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$	2	$E = \frac{M}{2}$
FeC_2O_4 (RA) (ferrous oxalate)	$Fe^{3+} + CO_2$	$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2 + 3e^-$	3	$E = \frac{M}{3}$

CONCEPT OF n-FACTOR OR VALENCY FACTOR

1. n_f = Number of e^- exchanged per molecule
   = Total change in ON per molecule
2. $E = \frac{M}{n_f}$
3. Number of eqv. = Number of moles × n_f

Example: Suppose that there are three atoms A, B, C and their oxidation number are 6, –1, –2, respectively. Then the molecular formula of compound will be

Sol. Since, the total charge on a free compound is zero. So

$+6 = (-1\times4) + (-2)$

$+6 = -6$

or $+6 = (-1\times2) + (-2\times2)$

So molecular formula, AB_4C or AB_2C_2.

LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction same no. of equivalent (or mill equivalent) of reactants react to give same no. of equivalent (or milli equivalents) of products separately.

According:

(*i*) $aA + bB \rightarrow mM + nN$

m.eq of A = m.eq of B = m.eq of M = m.eq of N

(*ii*) In a compound M_xN_y

m.eq of M_xN_y = m.eq of M = m.eq of N

Key Note

❖ **For Acid-base (Neutralization reaction) or redox reaction:**

$N_1V_1 = N_2V_2$ is always true

But $M_1V_1 = M_2V_2$ (may or may not be true)

$M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true where n terms represent n-factor)

REDOX TITRATION

Titrations based on redox processes are called redox titrations. In these titrations titrate/titrant are oxidising/ reducing agents. The calculations made in redox titrations are again based on law of chemical equivalence.

Titrate + Titrant → Products

Meq. of titrate = meq. of titrant (at equivalent point),

or $N_1V_1 = N_2V_2$

Titration Using Acidified $KMnO_4$

Use of $KMnO_4$ as oxidising agent in redox titrations was first made for the titration of Fe^{2+} ions. It is readily available and colour of its solution is too intense that an indicator is not ordinarily required and MnO_4^- ions act as self indicator. Titrations of MnO_4^- are usually carried out in acid medium.

Among the common mineral acids H_2SO_4, HCl and HNO_3 only H_2SO_4 is useful for providing acidic medium. HCl cannot be used since Cl^- are oxidised to Cl_2 by $KMnO_4$. On the other-hand HNO_3 itself acts as strong oxidising agent.

$$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

Some important titrations using $KMnO_4$ are given below:

(*a*) **$KMnO_4$ vs. oxalic acid:**

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

End point: Light pink colour of MnO_4^- solution, $KMnO_4$ acts as self indicator.

At equivalence point:

(i) 2m-mol $KMnO_4$ reacts with 5m–mol oxalic acid.

(ii) meq. of $KMnO_4$ = meq. of oxalic acid

$$N_{KMnO_4} \times V_{KMnO_4} = N_{\text{oxalic acid}} \times V_{\text{oxalic acid}}$$

(iii) $\frac{1}{2} \times M_{KMnO_4} \times V_{KMnO_4} = \frac{1}{5} \times M_{\text{oxalic acid}} \times V_{\text{Oxalic acid}}$

(*b*) **$KMnO_4$ vs. Fe^{2+} ions:**

Fe^{2+} is readily oxidised by MnO_4^- to Fe^{3+}. The reaction which takes place is given below:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 8H_2O$$

In the laboratory, for practical purposes ferrous ammonium sulphate is taken as a source of Fe^{2+} ions. In the determination of Fe content in iron ores, the whole iron content present in a definite amount of its solution is first converted into Fe^{2+} by using suitable reducing agent like $SnCl_2$.

End point: MnO_4^- acts as self indicator and light pink colour of solution indicates end point.

At equivalent point :

(i) 1mol MnO_4^- reacts with 5 mol Fe^{2+}.

(ii) Meq. of MnO_4^- = Meq. of Fe^{2+}

or $N_{KMnO_4} \times V_{KMnO_4} = N_{Fe^{2+}} \times V_{Fe^{2+}}$

or $5 \times M_{KMnO_4} \times V_{KMnO_4} = 1 \times M_{Fe^{2+}} \times V_{Fe^{2+}}$

$(\because N_{KMnO_4} = 5 \times M_{KMnO_4}, N_{Fe^{2+}} = M_{Fe^{2+}})$

(c) Estimation of Fe^{2+} and Fe^{3+} ions in a solution:

In this estimation, the solution is titrated twice. First without reduction in which only Fe^{2+} reacts and Fe^{3+} remains unreacted. In second step same volume of solution is taken. Fe^{3+} ions are reduced to Fe^{2+} and then titrated. Here

(i) In I step : Meq. of $KMnO_4$(let x) = Meq. of Fe^{2+}

(ii) In II step : Meq. $KMnO_4$(y) = Meq. of Fe^{2+} + Meq. of Fe^{3+}

(d) Analysis of sample containing oxalic acid and sodium oxalate:

Same volume of solution are titrated separately with NaOH and $KMnO_4$ solution

Meq. of NaOH = Meq. of oxalic acid

and Meq. of $KMnO_4$ = Meq. of oxalic acid +Meq. of sodium oxalate

Titration Using Acidified $K_2Cr_2O_7$

In volumetric analysis $Cr_2O_7^{2-}$ is also used commonly as oxidant yet weaker than MnO_4^-, Ce^{4+} etc. In most of its applications, it is reduced to Cr^{3+}.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$E_{Cr_2O_7^{2-}} = \frac{M_{Cr_2O_7^{2-}}}{6} = \frac{296}{6} = 49$$

These titrations are made in 1–2 N acid solution. In neutral or alkaline medium, it is not used. In alkaline medium orange $Cr_2O_7^{2-}$ changes to yellow CrO_4^{2-}.

Iodometric and Iodimetric Titration

Iodine acts as mild oxidising agent

These titrations fall into two categories :

(a) Iodimetry: In these titrations, standard I_2 solution is used to titrate easily oxidisable substances. It includes the estimations of thiosulphates, sulphite arsenite etc.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^-$$

$$AsO_3^{3-} + I_2 + H_2O \rightarrow AsO_4^{2-} + 2H^+ + 2I^-$$

$$H_2S + I_2 \rightarrow S + 2I^- + 2H^+$$

$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$$

$$N_2H_4 + 2I_2 \rightarrow N_2 + 4H^+ + 4I^-$$

(b) Iodometry: In iodiometric titrations an oxidising agent is allowed to react with excess of KI (or I^-) solution.

It includes the estimations of following species

$$2MnO_4^- + 10I^- + 16H^+ \rightleftharpoons Mn^{+2} + 5I_2 + 8H_2O$$

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$

The I_2 liberated is titrated with hypo solution ($Na_2S_2O_3$).

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

I_2, though insoluble in water, remains in solution containing KI as KI_3.

On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

Train Your Brain

Example 4: Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Sol. Normality (N) $= \frac{W \times 1000}{E \times V(mL)}$

where W=15.8 g, V=50 mL

$$E = \frac{\text{Molar mass of } KMnO_4}{\text{Valence factor}} = 158/5 = 31.6$$

So, N=10

Example 5: Calculate the normality of a solution containing 50 mL of 5M solution $K_2Cr_2O_7$ in acidic medium.

Sol. Normality (N) = Molarity × Valence factor = 5 × 6 = 30N

Example 6: Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \rightarrow Mn^{2+} + Cu^{2+} + SO_2$

Sol. From law of equivalence

equivalents of Cu_2S = equivalents of $KMnO_4$

moles of Cu_2S × v.f. = moles of $KMnO_4$ × v.f.

$1 \times 8 = n_2 \times 5$

$$n_2 = \frac{8}{5} = 1.6$$

Example 7: In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement?

Sol. Amount of NaOH present in 1000 mL of 0.15 M NaOH = 0.15 × 40 = 6 g

$\therefore$ 1 mL of this solution contain NaOH = 6×10^{-3} g

$\therefore$ 1.184 g of NaOH will be present in

$$= \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33 \text{ mL}$$

Example 8: Which of the following is/are correct ?

(*a*) g mole wt. = mol. wt. in g = wt. of 6.022×10^{23} molecules
(*b*) mole = N_A molecule = 6.02×10^{23} molecules
(*c*) mole = g-molecules
(*d*) None of the above

Sol. (*a*) g mole wt. = mol. wt. in g = wt. of 6.022×10^{23} molecules
(*b*) mole = N_A molecule = 6.02×10^{23} molecules
(*c*) mole = g-molecules

Example 9: Find the average and individual oxidation number of Fe & Pb in Fe_3O_4 & Pb_3O_4, respectively, which are mixed oxides.

Sol.

(*i*) Fe_3O_4 is mixture of FeO & Fe_2O_3 in 1 : 1 ratio so, individual oxidation number of Fe = +2 & +3

& average oxidation number = $\dfrac{1(+2)+2(+3)}{3} = 8/3$

(*ii*) Pb_3O_4 is a mixture of PbO & PbO_2 in 2 : 1 molar ratio so, individual oxidation number of Pb are +2 & +4 & average oxidation number of

$$Pb = \frac{2(+2)+1(+4)}{3} = 8/3$$

Concept Application

7. The number of moles of oxalate ion oxidized by one mole of $Cr_2O_7^{2-}$ ion in acidic medium.

(*a*) $\frac{6}{2}$ (*b*) $\frac{2}{5}$ (*c*) $\frac{3}{5}$ (*d*) $\frac{5}{3}$

8. How many moles of $KMnO_4$ are needed to oxidise a mixture containing 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium?

(*a*) $\frac{4}{5}$ (*b*) $\frac{5}{4}$
(*c*) $\frac{3}{4}$ (*d*) $\frac{5}{3}$

9. Equivalent weight of K_2CrO_4 when it reacts with $AgNO_3$ to give Ag_2CrO_4 is:

(*a*) Infinite (*b*) M
(*c*) $\frac{M}{2}$ (*d*) $\frac{M}{3}$

MISCELLANEOUS

1. n_f for species undergoes disproportionation

$= \dfrac{n_R \times n_o}{n_R \times n_o}$ (where n_R & no are n_f for Reduction & Oxidation processes)

2. Oxidation states:

$$\left.\begin{matrix} H_2SO_5 \\ H_2S_2O_8 \end{matrix}\right\} \delta(+6) \qquad CrO_5\} Cr(+6)$$
$$K_3CrO_5\} Cr(+5)$$
$$CaTiO_4\} Ti(+4)$$

BUILD A SUPPORT SYSTEM

- ❖ Strengthen relationships with family, friends, or mentors. When things get tough, having people to talk to and lean on makes it easier to cope.
- ❖ Create a habit of checking in with a close friend weekly. This support can boost morale and give you perspective when you're stressed.

Aarambh (Solved Examples)

1. Which of the following reaction represents the oxidising behaviour of H_2SO_4?

(*a*) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

(*b*) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

(*c*) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

(*d*) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

Sol. Oxidising nature ⇒ O.S. decreases

$$2HI + H_2\underbrace{\overset{+6}{S}O_4 \rightarrow I_2 + \overset{+4}{S}}_{\text{Reduction}}O_2 + 2H_2O$$

Therefore, option (*d*) is the correct answer.

2. In which of the following reaction H_2O_2 acts as reducing agent:

(*a*) $2FeCl_2 + 2HCl + H_2O_2 \rightarrow 2FeCl_3 + 2H_2O$

(*b*) $Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$

(*c*) $2HI + H_2O_2 \rightarrow 2H_2O + I_2$

(*d*) $H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$

Sol. $Cl_2 + H_2\overbrace{\overset{-1}{O_2} \rightarrow 2HCl + \overset{0}{O_2}}^{\text{Oxidation}}$

⇒ Reducing nature ⇒ O.S. Increases

Therefore, option (*b*) is the correct answer.

3. A sulphur containing species that can not be a reducing agent is:

(*a*) SO_2 (*b*) SO_3^{-2} (*c*) H_2SO_4 (*d*) $S_2O_3^{2-}$

Sol. $H_2\overset{+6}{S}O_4$

H_2SO_4 because sulphur has its maximum O.S. i.e. + 6

Therefore, option (*c*) is the correct answer.

4. Which of the following reaction involves neither oxidation nor reduction?

(*a*) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ (*b*) $Cr \rightarrow CrCl_3$

(*c*) $Na \rightarrow Na^+$ (*d*) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

Sol. $\overset{+6}{Cr}O_4^{2-} \rightarrow \overset{+6}{Cr_2}O_7^{2-}$

No change in O.S.

Therefore, option (*a*) is the correct answer.

5. Balance the following equations:

(*a*) $H_2O_2 + MnO_4^- \longrightarrow Mn^{+2} + O_2$ (acidic medium)

(*b*) $Zn + HNO_3\,(\text{dil.}) \longrightarrow Zn(NO_3)_2 + H_2O + NH_4NO_3$

(*c*) $CrI_3 + KOH + Cl_2 \longrightarrow K_2CrO_4 + KIO_4 + KCl + H_2O$

(*d*) $P_2H_4 \longrightarrow PH_3 + P_4$

(*e*) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow CaSiO_3 + P_4 + CO$

Sol. (*a*) $6H^+ + 5H_2O_2 + 2MnO_4^- \longrightarrow 2Mn^{+2} + 5O_2 + 8H_2O$

(*b*) $4Zn + 10HNO_3\,(\text{dil}) \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$

(*c*) $2CrI_3 + 64KOH + 27Cl_2 \longrightarrow 2K_2CrO_4 + 6KIO_4 + 54KCl + 32H_2O.$

(*d*) $6P_2H_4 \longrightarrow 8PH_3 + P_4$

(*e*) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO$

6. The number of electrons required to balance the following equation are:

$NO_3^- + 4H^+ \rightarrow 2H_2O + NO$

(*a*) 2 on right side (*b*) 3 on left side

(*c*) 3 on right side (*d*) 5 on left side

Sol. $\overset{+5}{N}O_3^- + 4H^+ \rightarrow 2H_2O + \overset{+2}{N}O$

So, $3e^- + \overset{+5}{N} \rightarrow \overset{+2}{N}$

Add 3 electrons on left side.

Therefore, option (*b*) is the correct answer.

7. $2KMnO_4 + 5H_2S + 6H^+ \rightarrow 2Mn^{2+} + 2K^+ + 5S + 8H_2O$. In the above reaction, how many moles of electrons would be involved in the oxidation of 1 mole of reductant?

(*a*) Two (*b*) Five

(*c*) Ten (*d*) One

Sol. $2K\overset{+7}{Mn}O_4 + 5H_2\underbrace{\overset{-2}{S} + 6H^+ \rightarrow 2\overset{+2}{Mn}{}^{2+} + 2K^+ + 5\overset{0}{S}}_{\text{Oxidation}} + 8H_2O$

H_2S ⇒ R.A. ⇒ Reductant

So, $\overset{-2}{S} \rightarrow \overset{0}{S} + 2e^-$

2 moles of electrons are involved in oxidation of 1 mole of reductant.

Therefore, option (*a*) is the correct answer.

8. In redox reaction:

$Fe + HNO_3 \rightarrow Fe(NO_3)_2 + NH_4NO_3 + H_2O$

the coefficient of HNO_3, $Fe(NO_3)_2$, NH_4NO_3 is:

(*a*) 1 : 10 : 4 (*b*) 10 : 4 : 1

(*c*) 4 : 10 : 1 (*d*) 10 : 1 : 4

Sol. $Fe + HNO_3 \longrightarrow Fe(NO_3)_2 + NH_4NO_3 + H_2O$

Half reaction method:

$Fe \longrightarrow Fe^{2+} + 2e^-$ ....(1) × 4

$NO_3^- + 10H^{\oplus} + 8e^{\ominus} \longrightarrow NH_4^{\oplus} + 3H_2O$ ...(2)

Equation (1) × 4 + (2)

$4Fe + NO_3^- + 10H^{\oplus} \longrightarrow 4Fe^{2+} + NH_4^{\oplus} + 3H_2O$

Add^n of spectator ion

$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

Therefore, option (*b*) is the correct answer.

9. Calculate the normality of a solution containing 13.4 g of Sodium oxalate in 100 mL solution.

Sol. $\text{Normality} = \dfrac{\text{wt. in g / eq. wt}}{\text{vol. of solution in litre}}$

Here, eq. wt. of $Na_2C_2O_4 = 134/2 = 67$

$\text{so } N = \dfrac{13.4/67}{100/1000} = 2N$

10. What volume of 6 M HNO_3 is needed to oxidize 8 g of Fe^{2+} to Fe^{3+}, where HNO_3 gets converted to NO?

(*a*) 8 mL (*b*) 7.936 mL

(*c*) 32 mL (*d*) 64 mL

Sol. Meq. of HNO_3 = Meq. of Fe^{2+}

or $6 \times 3 \times V = \dfrac{8}{56} \times 1000$

$V = 7.936$ mL

$$\underbrace{\overset{+5}{(NO_3^-} \rightarrow \overset{2+}{NO)}}_{\text{n-factor} = 3}$$

11. In the reaction, $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$, the eq. wt. of $Na_2S_2O_3$ is equal to its:

(*a*) Mol. wt. (*b*) Mol. wt./2

(*c*) 2 x Mol. wt. (*d*) Mol. wt./6

Sol. $\underset{\text{O.N.} = 2}{2S_2O_3^{2-}} + I_2 \longrightarrow \underset{\text{O.N.} = 2.5}{S_4O_6^{2-}} + 2I^{\ominus}$

v.f. = (0.5) × 2 = 1

$\Rightarrow \text{Eq. wt. } (S_2O_3^{2-}) = \dfrac{\text{Mol. wt.}}{1}$

Therefore, option (*a*) is the correct answer.

12. A sample of Pyrolusite (MnO_2) weighs 0.5 gm. To this solution, 0.594 gm of As_2O_3 and a dil. acid are added. After the reaction has ceased, As^{3+} in As_2O_3 is titrated with 45 mL of M/50 $KMnO_4$ solution. Calculate the % of MnO_2 in pyrolusite. (Molar mass of $Ar_2O_3 = 198$)

Sol. $MnO_2 + As_2O_3 \longrightarrow Mn^{2+} + AsO_4^{3-}$

0.5 gm 0.594 gm

For excess of As_2O_3

$As_2O_3 + MnO_4^- \longrightarrow Mn^{2+} + AsO_4^{3-}$

$E_{As_2O_3} = ?$

$(As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-)$

$\Rightarrow E_{As_2O_3} = \dfrac{198}{4}$

$\text{meq of } As_2O_3 \text{ taken} = \dfrac{0.594}{198/4} \times 1000 = 12$

meq of excess As_2O_3 = meq of $KMnO_4$

$= 45 \times \dfrac{1}{50} \times 5 = 4.5$

$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

Note that the number of electron transfer for As_2O_3 in two reactions is same.

so meq. of As_2O_3 used for $MnO_2 = 12 - 4.5 = 7.5$

meq of $MnO_2 = 7.5$

$\Rightarrow \dfrac{g}{87/2} \times 1000 = 7.5$

$(MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + 2e^-)$

$\Rightarrow g = 0.326$

$\% \, MnO_2 = \dfrac{0.326}{0.5} \times 100 = 65.25\%$

13. The neutralization of a solution of 1.2 gm of mixture of $H_2C_2O_4 . 2H_2O$ and $KHC_2O_4 . H_2O$ and some impurities which are neutral, consumed 40.0 mL of 0.25 N NaOH. On the other hand, on titration with $KMnO_4$ in acidic medium, 0.4 gm of mixture required 40.0 mL of 0.125 N $KMnO_4$. Find the molar ratio of the components.

Sol. Note that the mass of two samples is different in two titrations.

$\left.\begin{array}{l}\text{Let } x = \text{mmoles of } H_2C_2O_4 . 2H_2O \\ \text{and } y = \text{mmoles of } KHC_2O_4 . H_2O\end{array}\right\} \text{in 0.4 g sample}$

So mmoles of oxalic acid in 1.2gm sample = 3x and mmoles of bioxalate in 1.2 gm sample = 3y

1. **Neutralisation with NaOH:**

meq of $H_2C_2O_4 . 2H_2O$ + meq of $KHC_2O_4 . H_2O$ = meq of NaOH

$2 \times 3x + 1 \times 3y = 0.25 \times 40$

[oxalic acid has 2 H^+ ions while bioxalate has only 1 H^+]

$\Rightarrow 2x + y = \dfrac{10}{3}$ ...(i)

2. **Redox reaction with $KMnO_4$:**

meq of $H_2C_2O_4 . 2H_2O$ + meq of $KHC_2O_4 . H_2O$ = meq of $KMnO_4$

$2 \times x + 2 \times y = 0.125 \times 40$

$[HC_2O_4^- \longrightarrow 2CO_2 + H^+ + 2e^-]$

$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-]$

$\Rightarrow x + y = 2.5$ ...(ii)

Solve for x and y to get : $x = \dfrac{5}{6}$ and $y = \dfrac{5}{3}$

$\Rightarrow x : y = 1 : 2$

14. $KMnO_4$ solution is to be standardised by titration against As_2O_3(s). A 0.1097 g sample of As_2O_3 (M = 198) requires 26.10 ml of the $KMnO_4$ solution for its titration. What are the molarity and normality of the $KMnO_4$ solution?

Sol. $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$ (Reduction)

$As_2^{3+} \rightarrow 2As^{5+} + 4e^-$ (oxidation)

$\therefore$ Meq. of As_2O_3 = meq of $KMnO_4$

$\dfrac{0.1097}{\frac{198}{4}} \times 1000 = 26.10 \times N$ $(E_{As_2O_3} = M/4)$

$\therefore N_{KMnO_4} = 0.085$

$\therefore M_{KMnO_4} = \dfrac{0.085}{5} = 0.017$

15. 100 ml solution of FeC_2O_4 and $FeSO_4$ is completely oxidized by 60 ml of 0.02 M $KMnO_4$ in acid medium. The resulting solution is then reduced by Zn and dil.HCl. The reduced solution is again oxidized completely by 40ml 0.02 M $KMnO_4$. Calculate normality of FeC_2O_4 and $FeSO_4$ in mixture.

Sol. Consider the redox reaction

FeC_2O_4: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (Oxidation)

(N_1) $C_2^{3+} \rightarrow 2C^{4+} + 2e^-$ (Reduction)

$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2 + 3e^-$ (V.f. = 3)

$FeSO_4$: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (V.f. = 1)

(N_2)

$KMnO_4$: $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

$100\,(N_1 + N_2) = 60 \times 0.02 \times 5$

$(N_1 + N_2) = 3 \times 0.02$ ...(1)

The resulting solution now contains only Fe^{3+} ions because CO_2 escapes out. The solution is reduced to Fe^{2+} by Zn and dil.HCl.$KMnO_4$ oxidises these Fe^{2+} again, therefore meq. of Fe^{2+} from FeC_2O_4 + meq. of Fe^{2+} from $FeSO_4$ = meq. of $KMnO_4$

$$100\left(\frac{N_1}{3} + N_2\right) = 40 \times 0.02 \times 5$$

$$\left(\frac{N_1}{3} + N_2\right) = 2 \times 0.02 \quad ...(2)$$

$$\frac{2N_1}{3} = 0.02$$

$N_1 = 0.03, N_2 = 0.03$

16. 0.84 g iron containing X percent of iron was taken in a solution containing all the iron in ferrous state. The solution required X ml of a potassium dichromate solution for oxidation of iron content to ferric state. Calculate the strength (in g/L) of potassium dichromate solution.

Sol. $Fe \xrightarrow{\text{Valence factor}=2} Fe^{2+} + 2e^- \xrightarrow[\text{by } Cr_2O_7^{2-}]{\text{Valence factor}=1} Fe^{3+} + e^-$

(Oxidation)

$6e^- + Cr_2^{6+} \longrightarrow 2Cr^{3+}$ (Reduction)

$$W_{Fe} = \frac{0.84X}{100} \quad \text{(Given)}$$

Meq. of Fe^{2+} in solution (V.f. = 1) = meq. of $K_2Cr_2O_7$

$$\frac{0.84X}{100 \times 56} \times 1000 = X.N. \Rightarrow N = 0.15$$

$S_{K_2Cr_2O_7} = N \times E = 0.15 \times 49 = 7.35$ g/L

$\left(E = \frac{294}{6} = 49\right)$ (E = equivalent)

17. What mass of $K_2Cr_2O_7$ is required to produce 5.0 litre CO_2 at 75°C and 1.07 atm pressure from excess of oxalic acid. Also report the volume of 0.1 N NaOH required to neutralise the CO_2 evolved.

Sol. $Cr_2^{6+} + 6e^- \longrightarrow 2Cr^{3+}$

$C_2^{3+} \longrightarrow 2C^{4+} + 2e^-$

meq. of $K_2Cr_2O_7$ = meq. of CO_2 formed

= mole of $CO_2 \times 1000 \times 1$ (V.f for CO_2 = 1)

$$= \frac{PV}{RT} \times 1 \times 1000 = \frac{1.07 \times 5 \times 1000}{0.0821 \times 348} = 187.3$$

$$\therefore \frac{w_{K_2Cr_2O_7}}{M/6} \times 1000 = 187.3$$

$$\text{or } w_{K_2Cr_2O_7} = \frac{187.3 \times M}{6 \times 1000} = \frac{187.3 \times 294}{6 \times 1000}$$

$w = 9.18$ g ($M_{K_2Cr_2O_7} = 294$)

$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$ (V.f. for CO_2 = 2)

Also meq. of NaOH = meq. of CO_2

$0.1 \times V = 187.3 \times 2 \Rightarrow V = 3.746$ L

18. 2.480 g of $KClO_3$ are dissolved in conc.HCl and the solution was boiled. Chlorine gas evolved in the reaction was then passed through a solution of KI and liberated iodine was titrated with 100 ml of hypo.12.3 ml of same hypo solution required 24.6ml of 0.5 N iodine for complete neutralization. Calculate % purity of $KClO_3$ sample.

Sol. $2KClO_3 + 12\,HCl \longrightarrow 2KCl + 6H_2O + 6Cl_2$

$Cl_2 + 2KI \longrightarrow 2\,KCl + I_2$

Also meq. of I_2 = meq. of hypo = 100×1

$[\because N_{Hypo} \times 12.3 = 24.6 \times 0.5, \therefore N_{Hypo} = 1]$

$$\text{Also m M of } Cl_2 = \text{mM of } I_2 = \frac{100}{2} = 50$$

$$\text{Also mM of } KClO_3 = \frac{2 \times \text{mM of } Cl_2}{6} = \frac{2 \times 50}{6} = \frac{50}{3}$$

$$\therefore \frac{w_{KClO_3}}{122.5} \times 1000 = \frac{50}{3} \Rightarrow w_{KClO_3} = 2.042$$

$$\therefore \%\ KClO_3 = \frac{2.042}{2.48} \times 100 = 82.34\%$$

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. In which of the following reactions, the underlined substance has been oxidised?
   (*a*) $\underline{Br_2} + H_2S \rightarrow 2HBr + S$
   (*b*) $\underline{2HgCl_2} + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
   (*c*) $Cl_2 + \underline{2KI} \rightarrow 2KCl + I_2$
   (*d*) $\underline{2Cu^{2+}} + 4I^- \rightarrow Cu_2I_2 + I_2$

2. In which of the following reactions, H_2O_2 acts as a reducing agent?
   (*a*) $HOCl + H_2O_2 \xrightarrow{H^+} H_3O^+ + Cl^- + O_2$
   (*b*) $Mn^{2+} + H_2O_2 \xrightarrow{OH^-} Mn^{4+} + 2OH^-$
   (*c*) $2Fe^{2+} + H_2O_2 \xrightarrow{OH^-} 2Fe^{3+} + 2OH^-$
   (*d*) $PbS(s) + 4H_2O_2(aq) \xrightarrow{H^+} PbSO_4(s) + 4H_2O(l)$

3. When sulphur dioxide is passed in an acidified $K_2Cr_2O_7$ solution, the oxidation state of sulphur is changed from:
   (*a*) + 4 to 0 (*b*) + 4 to + 2
   (*c*) + 4 to + 6 (*d*) + 6 to + 4

4. In acidic medium, H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (–O–O–) bonds. Oxidation state of Cr in CrO_5 is:
   (*a*) +5 (*b*) +3 (*c*) +6 (*d*) –10

5. Oxidation number of S in H_2SO_5 is 6. This is observed because
   (*a*) There are five oxygen atoms in the molecule
   (*b*) The hydrogen atom is directly linked with non-metal
   (*c*) There is peroxide linkage in the molecule
   (*d*) The sulphur atom shows co-ordinate linkage

6. In the reaction,
   $IO_3^- + SO_2 + 4H_2O \rightarrow I_2 + SO_4^{2-} + 8H^+$
   the coefficient of SO_2 is:
   (*a*) 3 (*b*) 4 (*c*) 5 (*d*) 6

7. For the redox reaction
   $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$
   in the balanced equation, correct coefficient are

	MnO_4^-	Fe^{2+}	H^+
(*a*)	1	5	8
(*b*)	16	5	2
(*c*)	5	16	2
(*d*)	2	16	5

8. Which of the following is the most powerful oxidising agent?
   (*a*) F_2 (*b*) O_2 (*c*) Br_2 (*d*) I_2

ASSERTION AND REASON TYPE QUESTIONS

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
(*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
(*c*) Assertion is True but the Reason is False.
(*d*) Assertion is False but Reason is True.

9. **Assertion:** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.
   Reason: The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

10. **Assertion:** Bromide ion acts as a reducing agent in a reaction.
    $2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(aq) + 3\ BrO_3^-(aq) + 2OH^-(aq)$
    Reason: Oxidation number of bromine increases from –1 to 5.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the items in Column-I with relevant items in Column-II.

	Column-I		Column-II
A.	Ions having positive charge	(p)	+7
B.	The sum of oxidation number of all atoms in a neutral molecule	(q)	–1
C.	Oxidation number of hydrogen ion (H^+)	(r)	+1
D.	Oxidation number of Fluorine in NaF	(s)	0
E.	Ions having negative charge	(t)	Cation
		(u)	Anion

(*a*) A-(s); B-(p); C-(q); D-(r), E-(t)
(*b*) A-(u); B-(r); C-(q); D-(s) , E-(t)
(*c*) A-(p); B-(s); C-(u); D-(q), E-(r)
(*d*) A-(t); B-(s); C-(r); D-(q), E-(u)

12. Match the column-I with column-II.

	Column-I		Column-II
A.	$V_2O_5(s) + 5Ca(s) \rightarrow 2V(s) + 5CaO(s)$	(p)	Disproportionation reaction
B.	$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(l)$	(q)	Decomposition reaction
C.	$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$	(r)	Combustion reaction
D.	$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$	(s)	Displacement reaction

(*a*) A-(s); B-(r); C-(p); D-(q)
(*b*) A-(s); B-(q); C-(p); D-(r)
(*c*) A-(r); B-(s); C-(p); D-(q)
(*d*) A-(q); B-(s); C-(p); D-(r)

SHORT ANSWER TYPE QUESTIONS

13. Calculate the number of moles of MnO_4^- required by 1 mole of ferric oxalate in acidic medium for oxidation.

14. What volume of 0.1 M $KMnO_4$ is needed to oxidize 100 mg of FeC_2O_4 in acidic solution?

15. Which of the following species, do not show disproportionation reaction and why?

    ClO^-, ClO_2^-, ClO_3^- and ClO_4^-

    Also write reaction for each of the species that disproportionates.

16. In Oswald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g of ammonia and 20.00g of oxygen?

17. In the reaction $2KClO_3 \rightarrow 2KCl + 3O_2$, identify the species that is oxidized and the species that is reduced. Write down the balanced half-reactions for both oxidation and reduction.

18. The electrode potential for four metallic elements A, B, C and D are +0.80, −0.76, +0.12 and +0.34 V respectively. Arrange these elements in order of decreasing electron positive character. Give an explanation for the same.

LONG ANSWER TYPE QUESTIONS

19. Identify the type of reaction:
    (i) $3Mg + N_2 \rightarrow Mg_3N_2$
    (ii) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$
    (iii) $S_8 + 12OH^- \rightarrow 4S^{2-} + 2S_2O_3^{2-} + 6H_2O$
    (iv) $2H_2O \rightarrow 2H_2 + O_2$
    (v) $Fe + 2HCl \rightarrow FeCl_2 + H_2$

20. Calculate the oxidation number of:
    (i) C in C_3O_2
    (ii) Br in Br_3O_8
    (iii) S in $S_4O_6^{2-}$
    (iv) N in HN_3
    (v) Pb in $Pb(NO_3)_2$

21. (i) Balance the following redox reaction occurring in an acidic solution:

    $Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$.

    (ii) Balance a redox reaction in a basic solution:

    $H_2O_2(aq) + MnO_4^-(aq) \rightarrow MnO_2(s) + O_2(g) + OH^-(aq)$.

22. (i) How can we predict whether a redox reaction is taking place in an acidic, alkaline or neutral medium?

    (ii) An electrochemical cell is made by combining Al electrode having E^0 −1.66 V and Cu electrode having E^0 + 0.34 V. Which of these electrodes will work as a cathode and why?

    (iii) All decomposition reactions are not redox reactions. Explain.

23. Identify oxidizing and reducing agent in the reactions given below:
    (i) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
    (ii) $2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$
    (iii) $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$
    (iv) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
    (v) $V_2O_5 + 5Ca \rightarrow 2V + 5CaO$

CASE STUDY BASED QUESTIONS

24. You are a chemistry student conducting a laboratory experiment to explore various types of redox reactions. The laboratory instructor has provided you with several chemical substances and a set of instructions to perform specific redox reactions.

    Your task is to identify and classify the redox reactions as one of the following types: combination, decomposition, displacement, or combustion. Here are the substances provided for your experiment:

    Hydrogen Peroxide (H_2O_2): A colorless liquid commonly used as a disinfectant and bleaching agent.

    Potassium Permanganate ($KMnO_4$): A deep purple crystalline substance often used as an oxidizing agent in chemical reactions.

    Iron (Fe) Filings: Small pieces of iron metal that easily rust when exposed to air and moisture.

    Copper (Cu) Wire: A metal wire commonly used for electrical purposes.

    Hydrochloric Acid (HCl): A strong, corrosive acid used in various chemical processes.

    (i) You mix hydrogen peroxide (H_2O_2) with manganese dioxide (MnO_2) and observe the evolution of oxygen gas (O_2). What type of redox reaction is this?
    (*a*) Combination
    (*b*) Decomposition
    (*c*) Displacement
    (*d*) Combustion

    (ii) You immerse a piece of iron (Fe) in a solution of copper sulfate ($CuSO_4$), and over time, you notice the formation of copper (Cu) on the surface of the iron. What type of redox reaction is this?
    (*a*) Combination (*b*) Decomposition
    (*c*) Displacement (*d*) Combustion

    (iii) When you mix potassium permanganate ($KMnO_4$) with hydrochloric acid (HCl), you observe the reduction of the purple permanganate ion to a colorless solution. What type of redox reaction is this?
    (*a*) Combination (*b*) Decomposition
    (*c*) Displacement (*d*) Combustion

    (iv) You ignite a piece of paper, and it burns with a bright flame, releasing carbon dioxide (CO_2) and water vapor (H_2O). What type of redox reaction is involved in this?
    (*a*) Combination (*b*) Decomposition
    (*c*) Displacement (*d*) Combustion

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OXIDATION NUMBER, REDOX REACTIONS, REDUCING AGENT AND OXIDISING AGENT

1. In $Ni(CO)_4$, the oxidation state of Ni is:
(a) 4 (b) 0 (c) 2 (d) 8

2. The oxidation number of nitrogen in NH_2OH is:
(a) 0 (b) +1 (c) −1 (d) −2

3. The oxidation number of C in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are respectively:
(a) +4, +2, 0, −2, −4 (b) +2, +4, 0, −4, −2
(c) −4, −2, 0, +2, +4 (d) −2, −4, 0, +4,. +2

4. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is:
(a) +1 (b) +2 (c) +3 (d) +4

5. Oxidation number of C in HNC is:
(a) +2 (b) −3 (c) +3 (d) Zero

6. Oxidation number of carbon in carbon suboxide (C_3O_2) is :
(a) $\frac{+2}{3}$ (b) $\frac{+4}{3}$ (c) +4 (d) $\frac{-4}{3}$

7. Oxidation number of sulphur in $Na_2S_2O_3$ would be:
(a) +2 (b) +4 (c) −2 (d) 0

8. $\frac{-1}{3}$ oxidation state of nitrogen will be obtained in case of:
(a) Ammonia (NH_3) (b) Hydrazoic acid (N_3H)
(c) Nitric oxide (NO) (d) Nitrous oxide (N_2O)

9. Which one of the following is a redox reaction?
(a) $H_2 + Br_2 \rightarrow 2HBr$
(b) $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$
(c) $HCl + AgNO_3 \rightarrow AgCl + HNO_3$
(d) $NaOH + HCl \rightarrow NaCl + H_2O$

10. Which of the following change represents a disproportionation reaction (s)?
(a) $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$
(b) $Cu_2O + 2H^+ \rightarrow Cu + Cu^{2+} + H_2O$
(c) $2HCuCl_2 \xrightarrow[\text{Water}]{\text{dilution with}} Cu + Cu^{2+} + 4Cl^- + 2H^+$
(d) All of the above

11. The reaction $H_2S + H_2O_2 \rightarrow S + 2H_2O$ manifests:
(a) Oxidising action of H_2O_2
(b) Reducing nature of H_2O_2
(c) Acidic nature of H_2O_2
(d) Alkaline nature of H_2O_2

12. The compound that can work both as an oxidising as well as reducing agent is:
(a) $KMnO_4$ (b) H_2O_2
(c) $Fe_2(SO_4)_3$ (d) $K_2Cr_2O_7$

13. Select the example of disproportionation reaction
(a) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
(b) $NH_4NO_3 \rightarrow N_2O + 2H_2O$
(c) $4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$
(d) $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2Cl$

14. Which one of the following is not a redox reaction?
(a) $CaCO_3 \rightarrow CaO + CO_2$
(b) $2H_2 + O_2 \rightarrow 2H_2O$
(c) $Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2$
(d) $MnCl_3 \rightarrow MnCl_2 + \frac{1}{2}Cl_2$

15. In the reaction: $MnO_4^- + SO_3^{2-} + H^+ \rightarrow SO_4^{2-} + Mn^{2+} + H_2O$
(a) MnO_4^- and H^+ both are reduced
(b) MnO_4^- is reduced and H^+ is oxidised
(c) MnO_4^- is reduced and SO_3^{2-} is oxidised
(d) MnO_4^- is oxidised and SO_3^{2-} is reduced

16. Select the compound in which the oxidation number of oxygen is −1:
(a) H_2O (b) O_2F_2 (c) Na_2O (d) BaO_2

17. $I_2 + KI \rightarrow KI_3$
In the above reaction:
(a) Only oxidation takes place
(b) Only reduction takes place
(c) Both the above
(d) None of the above

18. Match List-I (compound) with List-II (Oxidation state of N) and select the correct answer using the codes given below the list:

List-I		List-II	
A.	KNO_3	(p)	− 1/3
B.	HNO_2	(q)	−3
C.	NH_4Cl	(r)	0
D.	NaN_3	(s)	+3
		(t)	+5

(a) (A-t), (B-s), (C-q), (D-p)
(b) (A-t), (B-q), (C-s), (D-p)
(c) (A-s), (B-t), (C-p), (D-r)
(d) (A-q), (B-r), (C-s), (D-t)

19. In the conversion of Br_2 to BrO_3^- the oxidation state of bromine changes from:
(a) 0 to 5 (b) 1 to 5 (c) 0 to −3 (d) 2 to 5

20. The sum of oxidation states of sulphur in $H_2S_2O_8$ is:
(a) +2 (b) +6 (c) +7 (d) +12

21. When H_2 reacts with Na, here H_2 acts as:
(a) Oxidising agent (b) Reducing agent
(c) Both (d) None of these

22. Which one is the oxidising agent in the reaction given below?
$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{-2} + H_2O$
(*a*) H^+ (*b*) $Cr_2O_7^{-2}$
(*c*) Cr^{++} (*d*) None of these

23. The oxidation number of arsenic atom in H_3AsO_4 is:
(*a*) –1 (*b*) –3 (*c*) +3 (*d*) +5

24. In substance $Mg(HXO_3)$, the oxidation number of X is:
(*a*) 0 (*b*) +2 (*c*) +3 (*d*) +4

25. Which statement is wrong?
(*a*) Oxidation number of oxygen is +1 in peroxides
(*b*) Oxidation number of oxygen is +2 in oxygen difluoride
(*c*) Oxidation number of oxygen is $-\frac{1}{2}$ in superoxides
(*d*) Oxidation number of oxygen is –2 in most of its compounds

26. In the reaction: $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$
HNO_3 acts as:
(*a*) An oxidising agent (*b*) An acid
(*c*) A reducing agent (*d*) None of these

27. The oxidation number of iron in potassium ferricyanide $K_3[Fe(CN)_6]$ is:
(*a*) Two (*b*) Six
(*c*) Three (*d*) Four

28. Iodine shows the highest oxidation state in the compound:
(*a*) KI (*b*) KI_3 (*c*) IF_5 (*d*) KIO_4

29. Oxidation number of Xe in XeF_5^- is:
(*a*) +1 (*b*) +2 (*c*) +3 (*d*) +4

30. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
Here Zn undergoes:
(*a*) Reduction
(*b*) Oxidation
(*c*) Both oxidation and reduction
(*d*) None of these

31. In the following reaction
$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$
(*a*) $FeCl_3$ is oxidant
(*b*) $FeCl_3$ & H_2S are oxidised
(*c*) $FeCl_3$ is oxidised & H_2S is reduced
(*d*) None of these

32. $MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O$
In the above reaction oxidation number of Mn changes from:
(*a*) +2 to – 3 (*b*) +4 to – 3
(*c*) +2 to + 3 (*d*) +4 to + 3

BALANCING OF REDOX REACTIONS

33. Choose the set of coefficients that correctly balances the following equation:
$x\,Cr_2O_7^{2-} + yH^+ + z\,e^- \rightarrow a\,Cr^{+3} + bH_2O$

	x	y	z	a	b
(*a*)	2	14	6	2	7
(*b*)	1	14	6	2	7
(*c*)	2	7	6	2	7
(*d*)	2	7	6	1	7

34. The value of n in: $MnO_4^- + 8H^+ + ne^- \rightarrow Mn^{2+} + 4H_2O$ is
(*a*) 5 (*b*) 4 (*c*) 3 (*d*) 2

35. What is the value of *n* in the following equation: $Cr(OH)_4^- + OH^- \rightarrow CrO_4^{2-} + H_2O + ne^-$?
(*a*) 3 (*b*) 6 (*c*) 5 (*d*) 2

36. For the redox reaction
$Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$ in basic medium, coefficients of Zn, NO_3^- and OH^- in the balanced equation respectively are:
(*a*) 4, 1, 7 (*b*) 7, 4, 1 (*c*) 4, 1, 10 (*d*) 1, 4, 10

37. In the following reaction the value of 'X' is
$H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + X$
(*a*) $4e^-$ (*b*) $3e^-$ (*c*) $2e^-$ (*d*) $1e^-$

38. In the reaction: $A^{-n_2} + xe^- \rightarrow A^{-n_1}$, here x will be
(*a*) $n_1 + n_2$ (*b*) $n_2 - n_1$ (*c*) $n_1 - n_2$ (*d*) $n_1 . n_2$

USE OF VALENCY FACTOR (n-FACTOR)

39. The number of mole of oxalate ions oxidised by one mole of MnO_4^- is:
(*a*) 1/5 (*b*) 2/5 (*c*) 5/2 (*d*) 5

40. How many moles of $KMnO_4$ are reduced by 1 mole of ferrous oxalate in acidic medium?
(*a*) $\frac{1}{5}$ (*b*) $\frac{5}{3}$ (*c*) $\frac{1}{3}$ (*d*) $\frac{3}{5}$

EQUIVALENT WEIGHT

41. Equivalent weight of N_2 in the change $N_2 \rightarrow NH_3$ is
(*a*) $\frac{28}{6}$ (*b*) 28 (*c*) $\frac{28}{2}$ (*d*) $\frac{28}{3}$

42. Equivalent weight of NH_3 in the change $N_2 \rightarrow NH_3$ is:
(*a*) $\frac{17}{6}$ (*b*) 17 (*c*) $\frac{17}{2}$ (*d*) $\frac{17}{3}$

43. The eq. wt. of iodine in, $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ is
(*a*) Mol. wt. (*b*) Mol. wt./2
(*c*) Mol. wt./4 (*d*) None of these

44. Molecular weight of $KBrO_3$ is M. What is its equivalent weight, if the reaction is:
$BrO_3^- \rightarrow Br^-$ (acidic medium)
(*a*) M (*b*) M/4 (*c*) M/6 (*d*) 6M

45. Equivalent wt. of H_3PO_4 in each of the reaction will be respectively:
$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$
$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$
$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O$
(*a*) 98, 49, 32.67 (*b*) 49, 98, 32.67
(*c*) 98, 32.67, 49 (*d*) 32.67, 49, 98

Prabal (JEE Main Level)

1. Oxidation number of S in $H_2S_2O_7$ is:
   (*a*) +4 (*b*) –6
   (*c*) –5 (*d*) +6

2. Oxidation number of S in H_2SO_5 is 6. This is observed, because:
   (*a*) There are five oxygen atoms in the molecule.
   (*b*) The hydrogen atom is directly linked with non-metal.
   (*c*) There is peroxide linkage in the molecule.
   (*d*) The sulphur atom shows co-ordinate linkage.

3. Oxygen has an oxidation state of +2 in the compound:
   (*a*) H_2O_2 (*b*) CO_2
   (*c*) H_2O (*d*) F_2O

4. Oxidation number of Fe in Fe_3O_4 is fractional because:
   (*a*) It is a mixed [Fe(+2), Fe(+4)] oxide.
   (*b*) It is a non-stoichiometric compound.
   (*c*) It is a mixed [Fe(+2), Fe(+3)] oxide.
   (*d*) None of the above.

5. The following equations are balanced atomwise and chargewise.
   (*i*) $Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \longrightarrow 2Cr^{3+} + 7H_2O + 3O_2$
   (*ii*) $Cr_2O_7^{2-} + 8H^+ + 5H_2O_2 \longrightarrow 2Cr^{3+} + 9H_2O + 4O_2$
   (*iii*) $Cr_2O_7^{2-} + 8H^+ + 7H_2O_2 \longrightarrow 2Cr^{3+} + 11H_2O + 5O_2$
   The precise equation/equations representing the oxidation of H_2O_2 is/are:
   (*a*) (*i*) only (*b*) (*ii*) only
   (*c*) (*iii*) only (*d*) All the three

6. Oxidation number of cobalt in $[Co(NH_3)_6]Cl_2Br$ is:
   (*a*) +6 (*b*) Zero (*c*) +3 (*d*) +2

7. State which of the following reactions is neither oxidation nor reduction:
   (*a*) $Na \rightarrow NaOH$
   (*b*) $Cl_2 \rightarrow Cl^- + ClO^-_3$
   (*c*) $P_2O_5 \rightarrow H_4P_2O_7$
   (*d*) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

8. Select the pair of oxidation processes,
   (A) $2Cu^{2+} \rightarrow Cu_2^{2+}$
   (B) $MnO_4^- \rightarrow Mn^{2+}$
   (C) $[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$
   (D) $2I^- \rightarrow I_2$
   (*a*) A, B (*b*) C, D (*c*) A, D (*d*) B, C

9. Phosphorus has the oxidation state of +3 in:
   (*a*) Ortho phosphoric acid (H_3PO_4)
   (*b*) Phosphorus acid (H_3PO_3)
   (*c*) Meta phosphoric acid (HPO_3)
   (*d*) Pyrophosphoric acid ($H_4P_2O_7$)

10. Which one of the following statements is not correct?
    (*a*) Oxidation state of S in $(NH_4)_2S_2O_8$ is +6
    (*b*) Oxidation number of Os in OsO_4 is +8
    (*c*) Oxidation state of S in H_2SO_5 is +8
    (*d*) Oxidation number of O in KO_2 is $-\frac{1}{2}$

11. Oxidation state of nitrogen is incorrectly given for:

	Compound	**Oxidation State**
(*a*)	$[Co(NH_3)_5Cl]Cl_2$	–3
(*b*)	NH_2OH	–1
(*c*)	$(N_2H_5)_2SO_4$	+2
(*d*)	Mg_3N_2	–3

12. $H_2MoO_4 \rightarrow MoO_2^+$. In the process, H_2MoO_4
    (*a*) Acts as a reducing agent.
    (*b*) Acts as an oxidising agent.
    (*c*) Acts both as a reducing and oxidising agent.
    (*d*) None of these.

13. Two oxidation states for chlorine are found in the compound:
    (*a*) $CaOCl_2$ (*b*) KCl
    (*c*) $KClO_3$ (*d*) Cl_2O_7

14. Which of the following example does not represent disproportionation:
    (*a*) $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
    (*b*) $2H_2O_2 \rightarrow 2H_2O + O_2$
    (*c*) $4KClO_3 \rightarrow 3KClO_4 + KCl$
    (*d*) $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

15. One mole of iron, when oxidised to +2 oxidation state gives up:
    (*a*) $1N_A$ electron
    (*b*) $2N_A$ electron
    (*c*) $3N_A$ electron
    (*d*) 0.5 mole of electron

16. In which of the following compounds iron has lowest oxidation state?
    (*a*) $FeSO_4(NH_4)_2SO_4.6H_2O$
    (*b*) $K_4Fe(CN)_6$
    (*c*) $Fe(CO)_5$
    (*d*) $Fe_{0.94}O$

17. In the reaction $xHI + yHNO_3 \longrightarrow NO + I_2 + H_2O$, upon balancing with whole number coefficients:
    (*a*) x = 3, y = 2 (*b*) x = 2, y = 3
    (*c*) x = 6, y = 2 (*d*) x = 6, y = 1

18. For the redox reaction $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$, the correct whole number stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively:
    (*a*) 2, 5, 16 (*b*) 16, 5, 2
    (*c*) 5, 16, 2 (*d*) 2, 16, 5

19. An example of redox process is:

(*a*) $CuSO_4 + Fe \rightarrow FeSO_4 + Cu$

(*b*) $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

(*c*) $CaO + 2HCl \rightarrow CaCl_2 + H_2O$

(*d*) $CaCO_3 \longrightarrow CaO + CO_2$

20. Consider the following statement in the reaction

$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$

(A) KI is oxidised to I_2

(B) KIO_3 is oxidised to I_2

(C) KIO_3 is reduced to I_2

(D) Oxidation number of I increases from (–1) in KI to zero in I_2

Among these statements

(*a*) A, C and D are correct. (*b*) A, B and D are correct.

(*c*) B and D are correct. (*d*) A alone is correct.

21. Balance the following equation and choose the quantity which is the sum of the coefficients of reactants and products:

$KMnO_4$ +....... H_2O_2 +....... $H_2SO_4 \longrightarrow$ .... $MnSO_4$ +....... O_2 +....... H_2O +....... K_2SO_4

(*a*) 26 (*b*) 23 (*c*) 28 (*d*) 22

22. In the redox reaction:

$x\,MnO + y\,PbO_2 + z\,HNO_3 \longrightarrow a\,HMnO_4 + b\,Pb(NO_3)_2 + c\,H_2O$

(*a*) $x = 2, y = 5, z = 10$ (*b*) $x = 2, y = 7, z = 8$

(*c*) $x = 2, y = 5, z = 8$ (*d*) $x = 2, y = 5, z = 5$

23. In the redox reaction:

$10FeC_2O_4 + x\,KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 20CO_2 + y\,MnSO_4 + 3\,K_2SO_4 + 24H_2O.$

The values of x and y are respectively:

(*a*) 6, 3 (*b*) 3, 6

(*c*) 3, 3 (*d*) 6, 6

24. The number of electrons lost or gained during the change:

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

(*a*) 2 (*b*) 4 (*c*) 6 (*d*) 8

25. $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O$

In the above reaction the oxidation state of N and chromium changes respectively as:

(*a*) – 3 to 0 and + 6 to + 3 (*b*) + 3 to 0 and + 3 to + 6

(*c*) – 4 to 0 and + 6 to + 2 (*d*) Unpredictable

26. How many electrons should A_2H_3 liberate so that in the new compound A shows –1/2 oxidation number- (E.N. of A > E.N. of H)

(*a*) 2 (*b*) 3

(*c*) 4 (*d*) 5

27. Number of moles of electrons produced per mole of $FeCr_2O_4$ in the following redox reaction is ......

$FeCr_2O_4 + KOH + O_2 \longrightarrow K_2CrO_4 + Fe_2O_3$

(*a*) 6 (*b*) 1 (*c*) 7 (*d*) 3

28. Carbon is in the lowest oxidation state in:

(*a*) CH_4 (*b*) CCl_4

(*c*) CF_4 (*d*) CO_2

29. x(g) of the metal gave y g of its oxide. Hence equivalent weight of the metal

(*a*) $\frac{y-x}{x} \times 8$ (*b*) $\frac{x}{(y-x)} \times 8$

(*c*) $\frac{x}{y} \times 8$ (*d*) $\frac{x+y}{x} \times 8$

30. Equivalent weight of Mn^{3+} in the following reaction is (Mn = 55)

$Mn^{3+} \rightarrow Mn^{2+} + MnO_2$

(*a*) 27.5 (*b*) 55

(*c*) 110 (*d*) 165

31. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weight of the metal is:

(*a*) 33.25 (*b*) 3.325

(*c*) 12 (*d*) 20

32. Equivalent weight of FeC_2O_4 in the change, $FeC_2O_4 \rightarrow Fe^{3+} + CO_2$ is

(*a*) M/3 (*b*) M/6

(*c*) M/2 (*d*) M/1

33. In the ionic equation, $2K^+BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O + 2K^+$, the equivalent weight of $KBrO_3$ will be (where M = molecular weight of $KBrO_3$):

(*a*) M/5 (*b*) M/2

(*c*) M/6 (*d*) M/4

34. If one mole of H_2SO_4 reacts completely with one mole of NaOH, equivalent weight of H_2SO_4 will be:

(*a*) 98 (*b*) 49

(*c*) 96 (*d*) 48

35. The equivalent weight of a metal is double that of oxygen. How many times is the weight of its oxide greater than weight of the metal?

(*a*) 1.5 (*b*) 2

(*c*) 0.5 (*d*) 3

36. $(NH_4)_3PO_4$ gets converted into NO_3^- and PH_3 on reacting with $KMnO_4$ in acidic medium. If 50 ml of 0.2 M $(NH_4)_3PO_4$ solution reacts completely with 16 ml of $KMnO_4$ solution, then normality of $KMnO_4$ solution is

(*a*) 5 (*b*) 8

(*c*) 10 (*d*) 20

37. The number of moles of NaOH required to completely react with 20 ml of 0.1 M NaH_2PO_3 solution and 40 ml of 0.1 M $NaHCO_3$ is ....

(*a*) 8×10^{-3} (*b*) 2×10^{-3}

(*c*) 4×10^{-3} (*d*) 6×10^{-3}

38. Which of the following compounds are arranged in increasing oxidation number of S?

(*a*) H_2SO_3, H_2S, H_2SO_4, $H_2S_2O_3$

(*b*) $H_2S_2O_3$, H_2SO_3, H_2S, H_2SO_4

(*c*) H_2S, H_2SO_3, H_2SO_4, $H_2S_2O_3$

(*d*) H_2S, $H_2S_2O_3$, H_2SO_3, H_2SO_4

39. Which of the following reaction is spontaneous oxidation–reduction reaction?

(*a*) $Mn^{+2} + 5Fe^{+3} + 4H_2O \rightarrow MnO_4^- + 5Fe^{+2} + 8H^+$

(*b*) $MnO_4^- + 5Fe^{+3} + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+2} + 4H_2O$

(*c*) $MnO_4^- + 5Fe^{+2} + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$

(*d*) $Mn^{+2} + 5Fe^{+2} + 4H_2O \rightarrow MnO_4^- + 5Fe^{+3} + 8H^+$

40. A compound contains atoms A, B and C. The oxidation number of A is +2, of B is +5 and of C is –2. The possible formula of the compound is:

(*a*) ABC_2 (*b*) $B_2(AC_3)_2$

(*c*) $A_3(BC_4)_2$ (*d*) $A_3(B_4C)_2$

41. The molar mass of $CuSO_4.5\,H_2O$ is 249. Its equivalent mass in the reaction (A) and (B) would be

(A) Reaction $CuSO_4 + KI \rightarrow$ product.

(B) Electrolysis of $CuSO_4$ solution.

(*a*) (A) 249 (B) 249 (*b*) (A) 124.5 (B) 124.5

(*c*) (A) 249 (B) 124.5 (*d*) (A) 124.5 (B) 249

INTEGER TYPE QUESTIONS

42. A solution containing 2.68×10^{-3} mol of A^{n+} ions requires 1.61×10^{-3} mol of MnO_4^- for the complete oxidation of A^{n+} to AO_3^- in acidic medium. What is the value of n?

43. 10 moles of Mohr's salt and $Fe_2(SO_4)_3$ mixture requires one litre of 1 M $K_2Cr_2O_7$ for complete oxidation. The number of mole of Mohr's salt in mixture is__________

44. 40 mL of X mol/litre formic acid is oxidised completely with 16 mL of 0.25 M oxidant. What is pH of formic acid? Assume 100% ionisation of acid.

45. The ratio of no. of oxygen atoms having –2 and –1 oxidation state in $S_2O_8^{2-}$ is __________

46. 10 mL of 0.2 M solution of $K_xH(C_2O_4)_y$ requires 8 mL of 0.2 M acidified $KMnO_4$ solution. The value of x is ______

47. Find out the % of oxalate ion in given sample of oxalate salt of which 0.3 g present in 100 mL of solution required 90 mL of (N/20) $KMnO_4$ for complete oxidation.

48. What is the coefficient for OH^- when the equation __Br_2 + __OH^- $\rightarrow$ __ Br^- + __BrO_3^- + __H_2O is balanced with the smallest integer coefficients?

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. Which of the following compound does not decolourize an acidified solution of $KMnO_4$?

(*a*) SO_2 (*b*) $FeCl_3$

(*c*) H_2O_2 (*d*) $FeSO_4$

2. What is equivalent mass of $(NH_4)_2Cr_2O_7$ in the change $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$?

(*a*) $\frac{M}{2}$ (*b*) $\frac{M}{3}$ (*c*) $\frac{M}{4}$ (*d*) $\frac{M}{6}$

3. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect in this reaction?

(*a*) Evolved I_2 is reduced (*b*) CuI_2 is formed

(*c*) $Na_2S_2O_3$ is oxidised (*d*) Cu_2I_2 is formed

4. 1 litre solution of KIO_3 of unknown molarity is given to titrate with KI in strong acid medium. 50 mL solution of KIO_3 requires 10 mL of 0.1 M KI for complete reduction to I_2. The molarity of KIO_3 solution is:

(*a*) 4×10^{-3} M (*b*) 4×10^{-4} M

(*c*) 4×10^{-5} M (*d*) 4×10^{-2} M

5. $Hg_5(IO_6)_2$ oxidizes KI to I_2 in acid medium and the other product containing iodine is K_2HgI_4. If the I_2 liberated in the reaction requires 0.004 mole of $Na_2S_2O_3$, the number of moles of $Hg_5(IO_6)_2$ that have reacted is:

(*a*) 10^{-3} (*b*) 10^{-4}

(*c*) 2.5×10^{-4} (*d*) 2.5×10^{-2}

6. If M represents molecular mass of Mn_3O_4 then what will be its equivalent mass if it undergoes disproportionation reaction as shown.

$Mn_3O_4 \rightarrow MnO_4^- + Mn^{2+}$

(*a*) $\frac{M}{13}$ (*b*) $\frac{M}{2}$ (*c*) $\frac{15M}{26}$ (*d*) $\frac{26M}{15}$

7. The CO in a 20.3 L sample of gas was converted to CO_2 by passing the gas over iodine pentoxide heated to 150° C:

$I_2O_5\,(s) + 5\,CO(g) \rightarrow 5\,CO_2(g) + I_2(g)$

The iodine distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M $Na_2S_2O_3$. The excess hypo was back-titrated with 2.16 mL of 0.00947 M I_2 solution. The milligrams of CO in 1 L of the original gas sample was therefore:

(*a*) 0.172 mg (*b*) 0.283 mg

(*c*) 0.349 mg (*d*) 0.506 mg

8. In the following conversion of sulphide of phosphorous

$P_4S_3 \rightarrow P_2O_5 + SO_2$

Equivalent weight of P_4S_3 (molecular weight = M) is:

(*a*) $\frac{M}{14}$ (*b*) $\frac{M}{18}$ (*c*) $\frac{M}{32}$ (*d*) $\frac{M}{38}$

9. Equivalent mass of $Ba(MnO_4)_2$ in acidic medium is: (where M stands for molar mass)

(*a*) M/5 (*b*) M/6 (*c*) M/10 (*d*) M/2

10. Equivalent mass of $Fe_{0.9}O$ in reaction with acidic $K_2Cr_2O_7$ is: (M = Molar mass)

(*a*) 7 M/10 (*b*) 10 M/7 (*c*) 7 M/9 (*d*) 9 M/7

11. Equivalent weight of oxalic acid salt in following reaction is: (Atomic masses: O = 16, C = 12, K = 39)

$H_2C_2O_4 + Ca(OH)_2 \longrightarrow CaC_2O_4 + H_2O$

(*a*) 90 (*b*) 45 (*c*) 64 (*d*) 128

12. Which of the following reactions do not involve oxdisation reduction?

I. $2Rb + 2H_2O \longrightarrow 2RbOH + H_2$

II. $2CuI_2 \longrightarrow 2CuI + I_2$

III. $4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

IV. $NH_4Br + KOH \longrightarrow KBr + NH_3 + H_2O$

(*a*) I, II (*b*) I, III (*c*) I, III, IV (*d*) III, IV

13. Ceric ammonium sulphate and potassium permanganate are used as oxidising agents in acidic medium for the oxidation of ferrous ammonium sulphate to ferric sulphate. The ratio of number of moles of ceric ammonium sulphate required per mole of ferrous ammonium sulphate to the number of moles of $KMnO_4$ required per mole of ferrous ammonium sulphate, is

(*a*) 5.0 (*b*) 0.2 (*c*) 0.6 (*d*) 2.0

14. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 ml oxidant. The resultant solution is neturalized by Na_2CO_3, acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 ml of 0.05 M $Na_2S_2O_3$ for complete reduction. Find out the mole ratio of Cu^{2+} and $C_2O_4^{2-}$ in the compound.

(*a*) 1 : 2 (*b*) 2 : 4 (*c*) 1 : 1 (*d*) 2 : 1

15. Equivalent weight of underlined substances in the given reactions are respectively

$\underline{K_4[Fe(CN)_6]} + MnO_4^- + H^+ \rightarrow Fe^{3+} + CO_2 + NO_3^- + Mn^{2+} + H_2O + K^+$

$Cu(s) + \underline{HNO_3}(aq) \rightarrow Cu(NO_3)_2(aq) + NO(g) + H_2O(\ell)$

{M_1 = Mol.wt. of $K_4[Fe(CN)_6]$

M_2 = Mol.wt. of HNO_3 }

(*a*) $\frac{M_1}{61}, \frac{M_2}{3}$ (*b*) $\frac{M_1}{1}, \frac{M_2}{3}$

(*c*) $\frac{M_1}{61}, \frac{4M_2}{3}$ (*d*) $\frac{M_1}{48}, \frac{M_2}{4}$

16. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 ml water 10 ml of this solution was reacted with excess of $FeCl_3$ solution and warmed to complete the reaction. Ferrous ions formed required 20 ml of $\frac{M}{50}$ $KMnO_4$ solution.

Given : $4Fe^{+3} + N_2H_4 \rightarrow N_2 + 4Fe^{+2} + 4H^+$

$MnO_4^- + 5Fe^{+2} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{+3} + 4H_2O$

The amount in gm of hydrazine sulphate in one litre is:

(*a*) 1.30 gm (*b*) 6.5 gm (*c*) 3.25 gm (*d*) 8.66 gm

17. Compounds in which oxidation state of at least one oxygen is (–1):

(1) H_2O_2 (2) O_2F_2

(3) H_2SO_5 (4) CrO_5

(5) $H_2S_2O_8$ (6) $[Na_2B_2H_4O_8]$

(*a*) 1,2,3,5 (*b*) 1,3,4,5,6

(*c*) 1,3,4 (*d*) 1,2,3,4,5,6

MULTIPLE CORRECT TYPE QUESTIONS

18. Substances which may be oxidized as well as reduced are

(*a*) HCl (*b*) HClO

(*c*) $HClO_3$ (*d*) $HClO_4$

19. Which of the following is a non-redox process?

(*a*) $SO_4^{2-} \rightarrow SO_3$ (*b*) $Cr_2O_7^{2-} \rightarrow CrO_4^{2-}$

(*c*) $PO_4^{3-} \rightarrow P_2O_7^{4-}$ (*d*) $C_2O_4^{2-} \rightarrow CO_2$

20. If mass of KHC_2O_4 (potassium acid oxalate) required to reduce 100 mL of 0.02 M $KMnO_4$ in acidic medium is x g and to neutralise 100 mL of 0.05 M $Ca(OH)_2$ is y g, then which of the following options may be correct?

(*a*) If x is 1 g then y is 2 g

(*b*) If x is 5.5g then y is 11 g

(*c*) If x is 2 g then y is 1 g

(*d*) If x is 11 g then y is 5.5 g

21. In the titration of $K_2Cr_2O_7$ and ferrous sulphate, following data is obtained:

V_1 mL of $K_2Cr_2O_7$ solution of molarity M_1 requires V_2 mL of $FeSO_4$ solution of molarity M_2.

Which of the following relations is/are true for the above titration?

(*a*) $6\,M_1V_1 = M_2V_2$ (*b*) $M_1V_1 = 6\,M_2V_2$

(*c*) $N_1V_1 = N_2V_2$ (*d*) $M_1V_1 = M_2V_2$

22. Choose the correct statement(s):

(*a*) 1 mole of MnO_4^- ion can oxidise 5 moles of Fe^{2+} ion in acidic medium.

(*b*) 1 mole of $Cr_2O_7^{2-}$ ion can oxidise 6 moles of Fe^{2+} ion in acidic medium.

(*c*) 1 mole of Cu_2S can be oxidised by 1.6 moles of MnO_4^- ion in acidic medium.

(*d*) 1 mole of Cu_2S can be oxidised by 1.33 moles of $Cr_2O_7^{2-}$ ion in acidic medium.

23. A quantity of 0.5 g of a metal nitrate gave 0.43 g of metal sulphate.

(*a*) The equivalent weight of the metal is 38.

(*b*) The equivalent weight of the metal is 76.

(*c*) The atomic weight of metal may be 76.

(*d*) The atomic weight of metal may be 19.

24. Which of the following samples of reducing agents is / are chemically equivalent to 25 mL of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water?

(*a*) 25 mL of 0.2 M $FeSO_4$ to be oxidized to Fe^{3+}

(*b*) 50 mL of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4

(*c*) 25 mL of 0.1 M H_2O_2 to be oxidized to H^+ and O_2

(*d*) 25 mL of 0.1 M $SnCl_2$ to be oxidized to Sn^{4+}

25. 250 ml of 1M I_2 is separately reacted with 0.5 M Cu_2S solution, 0.5 M CuS solution and 0.5 M $S_2O_3^{2-}$ solution, causing production of Cu^{+2} and SO_4^{2-} in the first two and $S_4O_6^{2-}$ in the last case along with iodide ions. Which of the following options is /are correct assuming 100% completion of the reaction?

(*a*) 100 ml of Cu_2S solution will be consumed.

(*b*) 125 ml of CuS solution will be consumed.

(*c*) 500 ml of $S_4O_6^{2-}$ solution will be consumed.

(*d*) Equivalent weight of I_2 in each of the reactions will be 127.

26. Which of the following statements is/are correct?

In the reaction $xCu_3P + yCr_2O_7^{2-} \longrightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$ (balanced with least possible all integral stoichiometic coefficients)

(*a*) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is also oxidised to PO_4^{3-}

(*b*) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is reduced to H_3PO_4

(*c*) In the conversion of Cu_3P to Cu^{2+} and H_3PO_4 total 11 electron are involved per molecule

(*d*) The value of x is 6

27. Which of the following statements is/are correct:

(*a*) Equivalent mass of Br_3O_8 in the following reaction is 23.
$Br_3O_8 + I^- + H^+ \rightarrow Br_2 + I_2 + H_2O$

(*b*) In case of oxialic acid ($H_2C_2O_4$), the average oxdation number and individual oxidation number of carbon have the same value.

(*c*) In case of iodimetric titration, KI is made to react with an oxidising agent and the liberated I_2 gas is made to titrate with hypo solution.

(*d*) Equivalent mass of Cu_3P in the following reaction is M/11 (where M = mol. mass)
$Cu_3P + KMnO_4 + H^+ \rightarrow Cu^{2+} + H_2PO_4^- + K^+ + Mn^{2+}$

28. Which of the following samples of reducing agent is/are chemically equivalent to 25 ml of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water?

(*a*) 25 ml of 0.2 M $FeSO_4$ to be oxidized to Fe^{3+}

(*b*) 50 ml of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4

(*c*) 25 ml of 0.4 M H_2O_2 to be oxidized to H^+ and O_2

(*d*) 25 ml of 0.1 M $SnCl_2$ to be oxidized to Sn^{4+}

COMPREHENSION TYPE QUESTIONS

Comprehension (Q. 29 to 31): For the reaction: $MnBr_2 + PbO_2 + HNO_3 \rightarrow HMnO_4 + Pb(BrO_3)_2 + Pb(NO_3)_2 + H_2O$
(Atomic masses: Mn = 55, Br = 80, Pb =208)

29. The equivalent weight of $MnBr_2$ is

(*a*) 107.5 (*b*) 215 (*c*) 12.65 (*d*) 19.55

30. The equivalent weight of PbO_2 is:

(*a*) 120 (*b*) 240 (*c*) 14.11 (*d*) 21.82

31. The equivalent weight of HNO_3 is:

(*a*) 63 (*b*) 55.6 (*c*) 31.5 (*d*) 111.18

Comprehension (Q. 32 to 34): A redox reaction involves oxidation and reduction simultanously by exchange of electrons. The species undergoing oxidation and reduction are reductant and oxidant respectively. In order to get n-factor for any oxidant or reductant change of oxidation number is to be find out.

32. The ion X^{+n} is oxidized to XO_3^- by MnO_4^- giving Mn^{2+} in acid solution. Given that 2.68×10^{-3} mole of X^{+n} requires 1.61×10^{-3} mole of MnO_4^-. What is the wt. of one g. equivalent of XCl_n for the above reaction if the atomic mass of X is 97.0?

(*a*) 80 (*b*) 84 (*c*) 168 (*d*) 72

33. How many gram HCl can be oxidized into free chlorine by 40 g. of $K_2Cr_2O_7$ in an acidic solution, the latter being reduced to Cr^{+3} ions? (Cr = 52, K = 39, O = 16)

(*a*) 29.579 (*b*) 29.785

(*c*) 29.795 gm (*d*) 29.859

34. Which of the following is not correct here?

(*a*) For the reaction $Cu_2S \longrightarrow CuO + SO_2$
$E_{Cu2S} = M/8$

(*b*) $aCu_2O + bNO_3^- + 14H^+ \longrightarrow Cu^{2+} + NO + 7H_2O$
Here a : b is 3 : 2

(*c*) $FeS_2 \longrightarrow Fe_2O_3 + SO_2$
Here $E = \frac{M}{11}$

(*d*) The value of n-factor of $Fe(SCN)_2$ where it oxidizes into Fe^{+3}, SO_4^{-2} and $(CN)_2$ is 10.

Comprehension (Q. 35 to 36): 632 g of sodium thiosulphate ($Na_2S_2O_3$) reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate to give cuprous compound which is dissolved in excess of sodium thiosulphate to form a complex compound sodium cuprothiosulphate ($Na_4[Cu_6(S_2O_3)_5]$).

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$
$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$
$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$$

Sodium cuprothiosulphaté

In this process, 0.2 mole of sodium cuprothiosulphate is formed. (O = 16, Na = 23, S = 32)

35. Moles of sodium thiosulphate reacted and unreacted after the reaction are respectively.

(*a*) 3 & 2 (*b*) 2 & 3

(*c*) 2.2 & 1.8 (*d*) 1.8 & 2.2

36. If instead of given amount of sodium thiosulphate, 2 moles of sodium thiosulphate along with 3 moles of Cu SO_4 were taken initially. Then moles of sodium cuprothiosulphate formed is

(*a*) 0 (*b*) 1 (*c*) 1.5 (*d*) 2

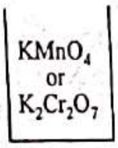
MATCH THE COLUMN TYPE QUESTIONS

37. **Container–I** may contain 1 mol $K_2Cr_2O_7$ or 1 mol $KMnO_4$ in acidic medium. This **container–I** is mixed with other **Container–II, III, IV** or **V**, due to which compound present in these containers undergo following half reaction.

$KI \longrightarrow IO_3^-, K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 3H_2O \longrightarrow CO_2$

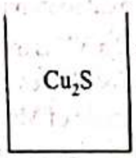
$Cu_2S \longrightarrow Cu^{2+} + SO_2$

$NH_4SCN \longrightarrow SO_4^{2-} + HCN$

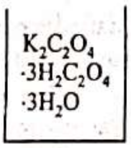


Container-I

Container-II



Container-III



Container-IV

Container-V

Column–I represents the two container which are mixed.

Column–II represents the number of moles of substance which reacts with 1 mol of substance (may be $KMnO_4$ or $K_2Cr_2O_7$) present in **container–I**.

Match the Column–I with Column–II.

	Column-I		Column-II
A.	Container–I + Container–III	p.	$\frac{3}{4}$
B.	Container–II + Container–I	q.	$\frac{5}{8}$
C.	Container–I + Container–V	r.	1
D.	Container–IV + Container–I	s.	$\frac{5}{6}$

(*a*) A → p,q; B → r,s; C → r,s; D → p,q
(*b*) A → s,r; B → p,q; C → r,s; D → p,q
(*c*) A → r,q; B → r,s; C → p,s; D → p,q
(*d*) A → s,q; B → r,p; C → r,s; D → p,q

38. Match the Column–I with Column–II.

	Column-I		Column-II
A.	$Sn^{+2} + MnO_4^-$ (acidic) 3.5 mole 1.2 mole	p.	Amount of oxidant available decides the number of electron transfer
B.	$H_2C_2O_4 + MnO_4^-$ (acidic) 8.4 mole 3.6 mole	q.	Amount of reductant available decides the number of electron transfer
C.	$S_2O_3^{-2} + I_2$ 7.2 mole 3.6 mole	r.	Number of electrons involved per mole of oxidant > Number of electrons involved per mole of reductant
D.	$Fe^{+2} + Cr_2O_7^{-2}$ (acidic) 9.2 mole 1.6 mole	s.	Number of electrons involved per mole of oxidant < Number of electrons involved per mole of reductant

(*a*) A → p,r; B → q,r; C → p,q,r; D → q,r
(*b*) A → s,r; B → p,q; C → r,s; D → p,q
(*c*) A → r,q; B → r,s; C → p,s; D → p,q
(*d*) A → s,q; B → r,p; C → r,s; D → p,q

39. To find molarity of 2 separate solutions of $KMnO_4$ and O_2 ($O_2 \longrightarrow O^{-2}$), a student titrated 20 ml of $KMnO_4$ (in neutral medium) and 10 ml of O_2 separately using 3 reagents A, B & C, performing 3 different experiments for $KMnO_4$ and O_2 each. He found molarity of $KMnO_4$ and O_2 as $\frac{1}{20}$M and $\frac{1}{10}$M respectively.

A, B & C are $FeCr_2O_4$, $CuFeS_2$, FeS respectively and their reactions are :

(A) $FeCr_2O_4 \longrightarrow K_2CrO_4 + Fe_2O_3$

(B) $CuFeS_2 \longrightarrow Cu^+ + Fe^{2+} + SO_2$

(C) $FeS \longrightarrow Fe^{+3} + SO_2$

Column-I represents solution of A, B, C used for titration

Column-II represents milli moles of A, B, C consumed with $KMnO_4$ or with O_2 or with both $KMnO_4$ as well as O_2.

	Column-I		Column-II
A.	$FeCr_2O_4$	p.	$\frac{3}{11}$
B.	$CuFeS_2$	q.	$\frac{3}{7}$
C.	FeS	r.	$\frac{4}{7}$
		s.	$\frac{4}{11}$

(*a*) A → q,r; B → p,s; C → q,r;
(*b*) A → s,r; B → p,q; C → r,s;
(*c*) A → r,q; B → r,s; C → p,s;
(*d*) A → s,q; B → r,p; C → r,s;

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INTEGER TYPE QUESTIONS

40. A 458 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+}. In the presence of fluoride ion, Mn^{2+} is titrated with 3 lit of $KMnO_4$ solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III). What was the % of Mn_3O_4 in the sample?

41. 80 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and volume made upto 250ml. 25 ml of this solution after taking usual precautions was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was produced. The iodine so evolved required 40 ml of 1 M of hypo solution. What is the approximate percentage purity of $CuSO_4$ solution? [Mol. wt. of $CuSO_4$ = 160]

42. Find the value of 2 × Ratio of moles of oxidant to reductant in the following reaction.

$$CrI_3 + Cl_2 + KOH \longrightarrow K_2CrO_4 + KIO_4 + KCl$$

43. A mixture of $NaHC_2O_4$ and $KHC_2O_4 . H_2C_2O_4$ is required for complete neutralization by 0.12 NaOH and 0.04 M $KMnO_4$ separately. The molar ratio of $NaHC_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ is:

44. A 1.100 g sample of copper ore is dissolved and the Cu^{2+} of it is treated with excess KI. The liberated I_2 requires 12.12 mL of 0.10 M $Na_2S_2O_3$ solution for titration. What is % copper by mass in the ore? (At mass of Cu = 63.6)

45. Given balanced chemical equation for oxidation of phosphorus (III) sulfide by nitric acid. The products include NO and SO_2. Find the value of a,b,c,d,e in the following equation.

$$a\,P_4S_6 + 44H^+ + b\,NO_3^- \rightarrow cNO + dH_3PO_4 + e\,SO_2 + 4H_2O$$

Write your answer as (a + b + c + d + e)

46. An equimolar mixture of CuO & Cu_2O is titrated with 100 ml 0.1 M $KMnO_4$ solution in acidic medium. Calculate millimoles of Cu^{2+} in final solution.

47. 1 litre solution containing 0.1 M $Na_2S_2O_3$ & 0.2 M IO_4^- is titrated with I_2 according to following reaction.

$$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + I^-$$

$$IO_4^- + I_2 \longrightarrow IO_3^-$$

Calculate millimoles of I_2 consumed?

48. 20 ml of $KMnO_4$ solution completely reacts with 10 ml solution of 1M FeS_2 and 2M CuS to produce Cu^{+2}, Fe^{+3}, SO_2. Calculate Normality of $KMnO_4$ solution?
[multiply final answer by 100]

49. 0.19 mole of $CuSO_4$ was added to excess of KI solution and liberated I_2 was reacted with hypo. How much volume (in ml) of 1M Hypo is required to react completely with liberated I_2?

$$CuSO_4 + KI \rightarrow Cu_2I_2 + I_2 + K_2SO_4$$

$$I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + NaI$$

50. In 20 ml of solution of $NaBrO_3$, 168 ml of SO_2 gas (measured at 0°C and 1 atm) is passed, which reduced some $NaBrO_3$ to NaBr. The resulting solution required 50 ml of 0.2 N solution of a reducing agent for complete reduction of remaining $NaBrO_3$ into NaBrO. The concentration (in g/L) of $NaBrO_3$ solution taken was [Br = 81, Na = 23, O = 16]

51. To find formulae of a compound we can titrate NH_3 in the compound with standardized acid, like

$$Cr(NH_3)_xCl_3(aq) + xHCl(aq) \rightarrow xNH_4^+(aq) + Cr^{3+}(aq) + (x+3)\,Cl^-(aq)$$

Assume that 20 ml of 1.5 MHCl is used to titrate 1.3025 gm of $Cr(NH_3)_xCl_3$, what is value of x? (Cr = 55)

52. An important oxidation-reduction reaction used to determine very small amounts of O_3 and other oxidants in polluted air involves oxidation of iodide ion :

$$2I^- + O_3 + H_2O \longrightarrow 2OH^- + I_2 + O_2$$

The solution is acidified and the I_2 is titrated with sodium thiosulphate solution using starch indicator. One litre of a mixture of O_3 and O_2 at STP was allowed to react with an excess of acidified solution of KI and I_2 liberated required value of 40 mL of M/10 sodium thiosulphate solution. What is the Value of (mole or volume percentage of ozone × 100) in the mixture?

NUMERICAL TYPE QUESTIONS

53. What mass (in g) of $Na_2S_2O_3 \cdot 5H_2O$ is needed to make 500 cm^3 of 0.200 N solution for the reaction:

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$? **(Upto one decimal place)**

54. 2.5 g sample of copper is dissolved in excess of H_2SO_4 to prepare 100 mL of 0.02 M $CuSO_4$ (aq.). 10 mL of this solution is iodometrically titrated and requires 2 mL of 0.1 M hyposolution. Calculate percentage purity of sample.
(Upto two decimal place)

PYQ's (Past Year Questions)

OXIDATION NUMBER AND ITS APPLICATION

1. From the given list, the number of compounds with + 4 oxidation state of Sulphur ______.

SO_3, H_2SO_3, $SOCl_2$, SF_4, $BaSO_4$, $H_2S_2O_7$

[27 Jan, 2024 (Shift-I)]

2. Which of the following cannot function as an oxidising agent?

[27 Jan, 2024 (Shift-II)]

(*a*) N^{3-} (*b*) SO_4^{2-}

(*c*) BrO_3^- (*d*) MnO_4^-

[illegible] the reaction given below:

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

$S_2O_3^{2-} + 5Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 4Br^- + 10H^+$

Which of the following statement justifies the above dual behaviour of thiosulphate? **[08 April, 2024 (Shift-I)]**

(*a*) Bromine undergoes oxidation and iodine undergoes reduction by iodine in these reactions

(*b*) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reaction

(*c*) Bromine is a stronger oxidant than iodine

(*d*) Bromine is a weaker oxidant than iodine

4. In Chromyl chloride, the oxidation state of chromium is (+). **[15 April, 2023 (Shift-I)]**

5. A sample of a metal oxide has formula $M_{0.83}O_{1.00}$. The metal M can exist in two oxidation states +2 and +3. In the sample of $M_{0.83}O_{1.00}$, the percentage of metal ions existing in +2 oxidation state is _____ % (nearest integer) **[31 Jan, 2023 (Shift-II)]**

6. In ammonium-phosphomolybdate, the oxidation state of Mo is + (____) **[6 April, 2023 (Shift-I)]**

7. In neutral or faintly alkaline medium, $KMnO_4$ being a powerful oxidant can oxidize, thiosulphate almost quantitatively, to sulphate. In this reaction, overall change in oxidation state of manganese will be: **[29 July, 2022 (Shift-I)]**

(*a*) 5 (*b*) 1 (*c*) 0 (*d*) 3

8. The difference in oxidation state of chromium in chromate and dichromate salts is________. **[24 June, 2022 (Shift-I)]**

9. In the titration of $KMnO_4$ and oxalic acid in acidic medium, the change in oxidation number of carbon at the end points ____________. **[27 July, 2022 (Shift-I)]**

10. The common positive oxidation states for an element with atomic number 24, are: **[17 March, 2021 (Shift-II)]**

(*a*) +1 and +3 to +6 (*b*) +1 and +3

(*c*) +2 to +6 (*d*) +1 to +6

11. Identify the process in which change in the oxidation state is five: **[25 July, 2021 (Shift-II)]**

(*a*) $CrO_4^{2-} \rightarrow Cr^{3+}$ (*b*) $MnO_4^- \rightarrow Mn^{2+}$

(*c*) $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ (*d*) $C_2O_4^{2-} \rightarrow 2CO_2$

12. Oxidation number of potassium in K_2O, K_2O_2 and KO_2 respectively is **[7 Jan, 2020 (Shift-I)]**

(*a*) +1, +2 and +4 (*b*) +1, +1 and $+\frac{1}{2}$

(*c*) +1, +1 and +1 (*d*) +1, +4 and +2

13. The compound that cannot act both as oxidising and reducing agent is: **[9 Jan, 2020 (Shift-I)]**

(*a*) HNO_2 (*b*) H_3PO_4 (*c*) H_2SO_3 (*d*) H_2O_2

14. Consider the following molecules : Br_3O_8, F_2O, $H_2S_4O_6$, $H_2S_5O_6$, and C_3O_2. Count the number of atoms existing in their zero oxidation state in each molecule. Their sum is ____. **[JEE Adv 2023]**

TYPES OF REDOX REACTIONS AND BALANCING OF REDOX REACTIONS

15. Chlorine undergoes disproportionation in alkaline medium as shown below:

$aCl_2(g) + bOH^-(aq) \rightarrow cClO^-(aq) + dCl^-(aq) + eH_2O(l)$

The values of a, b, c and d in a balanced redox reaction are respectively: **[29 Jan, 2024 (Shift-I)]**

(*a*) 1, 2, 1 and 1 (*b*) 2, 2, 1 and 3

(*c*) 3, 4, 4 and 2 (*d*) 2, 4, 1 and 3

16. Total number of species from the following which can undergo disproportionation reaction ________.

H_2O_2, ClO_3^-, P_4, Cl_2, Ag, Cu^{+1}, F_2, NO_2, K^+ **[30 Jan, 2024 (Shift-II)]**

17. Given below are two statements:

Statement-I: S_8 solid undergoes disproportionation reaction under alkaline conditions to form S^{2-} and $S_2O_3^{2-}$

Statement-II: ClO_4^- can undergo disproportionation reaction under acidic condition.

In the light of the above statements, choose the most appropriate answer from the options given below: **[31 Jan, 2024 (Shift-II)]**

(*a*) Statement-I is correct but statement-II is incorrect.

(*b*) Statement-I is incorrect but statement-II is correct

(*c*) Both statement-I and statement-II are incorrect

(*d*) Both statement-I and statement-II are correct

18. Match **List-I** with the **List-II**

	List-I **Reaction**		**List-II** **Type of redox reaction**
A.	$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$	I.	Decomposition
B.	$2Pb(NO_3)_{2(s)} \rightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$	II.	Displacement
C.	$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq.)} + H_{2(g)}$	III.	Disproportionation
D.	$2NO_{2(g)} + 2OH^-_{(aq.)} \rightarrow NO^-_{2(aq.)} + NO^-_{3(aq.)} + H_2O_{(l)}$	IV.	Combination

Choose the **correct** answer from the options given below: **[06 April, 2024 (Shift-II)]**

(*a*) (A)-(I), (B)-(II), (C)-(III), (D)-(IV)

(*b*) (A)-(III), (B)-(II), (C)-(I), (D)-(IV)

(*c*) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

(*d*) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

19. Iron (III) catalyses the reaction between iodide and persulphate ions, in which

A. Fe^{3+} oxidises the iodide ion

B. Fe^{3+} oxidises the persulphate ion

C. Fe^{2+} reduces the iodide ion

D. Fe^{2+} reduces the persulphate ion

Choose the **most appropriate** answer from the options given below: **[08 April, 2024 (Shift-I)]**

(*a*) B and C only (*b*) B only

(*c*) A only (*d*) A and D only

20. $2IO_3^- + xI^- + 12H^+ \rightarrow 6I_2 + 6H_2O$. What is the value of x? **[8 April, 2023 (Shift-I)]**

(*a*) 12 (*b*) 2

(*c*) 6 (*d*) 10

21. Which of the following options are correct for the reaction $2[Au(CN)_2]^-_{(aq)} + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{-2}_{(aq)}$? **[6 April, 2023 (Shift-I)]**

A. Redox reaction B. Displacement reaction

C. Decomposition reaction D. Combination reaction

Choose the correct answer from the options given below:

(*a*) A and B only (*b*) A only

(*c*) C and D only (*d*) A and D only

22. Which one of the following is an example of disproportionation reaction? **[26 June, 2022 (Shift-II)]**

(*a*) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(*b*) $MnO_4^- + 4H^+ + 4e^- \rightarrow MnO_2 + 2H_2O$

(*c*) $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(*d*) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

23. Which of the given reactions is not an example of disproportionation reaction? **[26 July, 2022 (Shift-I)]**

(*a*) $2H_2O_2 \rightarrow 2H_2O + O_2$

(*b*) $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

(*c*) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

(*d*) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

24. Match the List-I with List-II. **[1 Sept, 2021 (Shift-II)]**

	List-I		List-II
A.	Hydrolysis	I.	$2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au(sol) + 3HCOOH + 6HCl$
B.	Reduction	II.	$As_2O_3 + 3H_2S \rightarrow As_2S_3(sol) + 3H_2O$
C.	Oxidation	III.	$SO_2 + 2H_2S \rightarrow 3S(sol) + 2H_2O$
D.	Double Decomposition	IV.	$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3(sol) + 3HCl$

Choose the most appropriate answer from the options given below.

(*a*) (A)-(IV), (B)-(II), (C)-(III), (D)-(I)

(*b*) (A)-(I), (B)-(II), (C)-(IV), (D)-(III)

(*c*) (A)-(I), (B)-(III), (C)-(II), (D)-(IV)

(*d*) (A)-(IV), (B)-(I), (C)-(III), (D)-(II)

25. The species given below that does NOT show disproportionation reaction is: **[20 July, 2021 (Shift-I)]**

(*a*) BrO^- (*b*) BrO_3^- (*c*) BrO_2^- (*d*) BrO_4^-

26. The reaction of sulphur in alkaline medium is given below

$S_8(s) + aOH^-(aq) \rightarrow bS^{2-}(aq) + cS_2O_3^{2-}(aq) + dH_2O(l)$

The values of 'a' is __________. (Integer answer) **[24 Feb, 2021 (Shift-I)]**

27. The redox reaction among the following is: **[7 Jan, 2020 (Shift-II)]**

(*a*) Reaction of $[Co(H_2O)_6]Cl_3$ with $AgNO_3$

(*b*) Formation of ozone from atmospheric oxygen in the presence of sunlight

(*c*) Combination of dinitrogen with dioxygen at 2000 K

(*d*) Reaction of H_2SO_4 with NaOH

28. Consider the following equations:

$2Fe^{2+} + H_2O_2 \rightarrow xA + yB$ (in basic medium)

(in acidic medium)

$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow x'C + y'D + z'E$

(in acidic medium) **[4 Sept, 2020 (Shift-II)]**

The sum of the stoichiometric coefficients x, y, x′, y′ and z′ for products A, B, C, D and E, respectively, is ________

29. An example of a disproportionation reaction is: **[12 April, 2019 (Shift-I)]**

(*a*) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(*b*) $2MnO^-_4 + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(*c*) $2CuBr \rightarrow CuBr_2 + Cu$

(*d*) $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

REDOX REACTIONS, ELECTRODE PROCESSES AND TITRATIONS

30. If 50 mL of 0.5 M oxalic acid is required to neutralise 25 mL of NaOH solution, the amount of NaOH in 50 mL of given NaOH solution is _____ g. **[29 Jan, 2024 (Shift-II)]**

31. Given below are two statements:

Statement-I: Potassium hydrogen phthalate is a primary standard for standardisation of sodium hydroxide solution.

Statement-II: In this titration phenolphthalein can be used as indicator.

In the light of the above statements, choose the **most appropriate** answer from the options given below: **[01 Feb, 2024 (Shift-I)]**

(*a*) Both Statement-I and Statement-II are correct

(*b*) Statement-I is correct but Statement-II is incorrect

(*c*) Statement-I is incorrect but Statement-II is correct

(*d*) Both Statement-I and Statement-II are incorrect

32. Only 2 mL of $KMnO_4$ solution of unknown molarity is required to reach the end point of a titration of 20 mL of oxalic acid (2 M) in acidic medium. The molarity of $KMnO_4$ solution should be ________ M. **[04 April, 2024 (Shift-I)]**

33. Identify the **incorrect** statements regarding primary standard of titrimetric analysis **[09 April, 2024 (Shift-I)]**

(A) It should be purely available in dry form.

(B) It should not undergo chemical change in air.

(C) It should be hygroscopic and should react with another chemical instantaneously and stoichiometrically.

(D) It should be readily soluble in water.

(E) $KMnO_4$ & NaOH can be used as primary standard.

Choose the **correct** answer from the options given below:

(*a*) (C) and (D) only (*b*) (B) and (E) only

(*c*) (A) and (B) only (*d*) (C) and (E) only

34. When equal volume of 1M HCl and 1M H_2SO_4 are separately neutralised by excess volume of 1M NaOH solution. x and y kJ of heat is liberated respectively. The value of y/x is ________. **[09 April, 2024 (Shift-I)]**

35. Given below are two statements:

Statement-I: In redox titration, the indicators used are sensitive to change in pH of the solution.

Statement-II: In acid-base titration, the indicators used are sensitive to change in oxidation potential.

[8 April, 2023 (Shift-II)]

In the light of the above statements, choose the most appropriate answer from the options given below

(*a*) Both Statement-I and Statement-II are correct.

(*b*) Statement-I is incorrect but Statement-II is correct.

(*c*) Statement-I is correct but Statement-II is incorrect.

(*d*) Both Statement-I and Statement-II are incorrect.

36. 20 mL of calcium hydroxide was consumed when it was reacted with 10 mL of unknown solution of H_2SO_4. Also 20 mL standard solution of 0.5 M HCl containing 2 drops of phenolphthalein was titrated with calcium hydroxide, the mixture showed pink colour when burette displayed the value of 35.5 mL whereas the burette showed 25.5 mL initially. The concentration of H_2SO_4 is ________ M (Nearest integer) **[13 April, 2023 (Shift-I)]**

37. Given below are two statements : One is labelled as **Assertion (A)** and the other is labelled as **Reason (R).**

[28 July, 2022 (Shift-II)]

Assertion (A): Permanganate titrations are not performed in presence of hydrochloric acid.

Reason (R): Chlorine is formed as a consequence of oxidation of hydrochloric acid.

In the light of the above statements, choose the correct answer from the options given below

(*a*) Both (A) and (R) are true and (R) is the correct explanation of (A)

(*b*) Both (A) are (R) are true but (R) is NOT the correct explanation of (A)

(*c*) (A) is true but (R) is false

(*d*) (A) is false but (R) is true

38. 20 mL of 0.02 M $K_2Cr_2O_7$ solution is used for the titration of 10 mL of Fe^{2+} solution in the acidic medium. The molarity of Fe^{2+} solution is ________ $\times 10^{-2}$ M. (Nearest Integer) **[27 July 2022 (Shift-I)]**

39. In basic medium CrO_4^{2-} oxidises $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes into $Cr(OH)_4^-$. The volume of 0.154 M CrO_4^{2-} required to react with 40mL of 0.25 M $S_2O_3^{2-}$ is ____mL. (Rounded – off to the nearest integer)

[25 Feb, 2021 (Shift-I)]

40. 10.0 mL of Na_2CO_3 solution is titrated against 0.2 M HCl solution. The following titre values were obtained in 5 readings: **[18 March, 2021 (Shift-II)]**

4.8 mL, 4.9 mL 5.0 mL 5.0 mL and 5.0 mL

Based on these readings, and convention of titrimetric estimation, the concentration of Na_2CO_3 solution is ________ mM. (Round off to the nearest integer).

41. When 10 ml of an aqueous solution of Fe^{2+} ions was titrated in the presence of dil H_2SO_4 using diphenylamine indicator, 15 mL of 0.02 M solution of $K_2Cr_2O_7$ was required to get the end point. The molarity of the solution containing Fe^{2+} ions is x $\times 10^{-2}$ M. The value of x is. (Nearest integer) **[25 July, 2021 (Shift-I)]**

42. 10.0 ml of 0.05 M $KMnO_4$ solution was consumed in a titration with 10.0 mL of given oxalic acid dehydrate solution. The strength of given oxalic acid solution is ________ $\times 10^{-2}$ g/L **[27 July, 2021 (Shift-II)]**

(Round off to the Nearest Integer).

43. When 35 mL of 0.15 M lead nitrate solution is mixed with 20mL of 0.12 M chromic sulphate solution, ________ $\times 10^{-5}$ moles of lead sulphate precipitate out.

(Round off to the nearest integer).

[16 March 2021 (Shift-I)]

44. 15 mL of aqueous solution of Fe^{2+} in acidic medium completely reacted with 20 ml. of 0.03 M aqueous $Cr_2O_7^{2-}$. The molarity of the Fe^{2+} solution is ________ $\times 10^{-2}$ M

(Round off to the nearest integer).

[17 March 2021 (Shift-I)]

45. The exact volumes of 1 M NaOH solution required to neutralize 50 mL. of 1M H_3PO_3 solution and 100 mL of 2M H_3PO_2 solution respectively, are: **[16 March, 2021 (Shift-II)]**

(*a*) 100 mL and 50 mL (*b*) 100 mL and 200 mL

(*c*) 50 mL and 50 mL (*d*) 100 mL and 100 mL

46. The strength of an aqueous NaOH solution is most accurately determined by titrating: (Note : consider that an appropriate indicator is used) **[8 Jan, 2020 (Shift-I)]**

(*a*) Aq. NaOH in a burette and aqueous oxalic acid in a conical flask

(*b*) Aq. NaOH in a pipette and aqueous oxalic acid in a burette

(*c*) Aq. NaOH in a volumetric flask and concentrated H_2SO_4 in a conical flask

(*d*) Aq. NaOH in a burette and concentrated H_2SO_4 in a conical flask

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PW Challengers

PASSAGE I

A mixture of metallic iron with freshly prepared iron (II) and iron (III) oxides was heated in a closed vessel in the atmosphere of di-hydrogen. An amount of 4.72 g of the mixture when reacted, yields 3.92 g of iron and 0.90 g of water.

When the same amount of the mixture was allowed to react with an excess of a copper(II) sulphate solution, 4.96 g of a solid mixture were obtained.

1. Calculate the volume (in cm^3) of 7.3 % hydrochloric acid (ρ = 1.03 g cm^{-3}) which is needed for a total dissolution of 4.72 g of the starting mixture.
2. What volume (in cm^3) of a gas at STP is released?

   Relative atomic masses:

   $A_r(O) = 16$; $A_r(S) = 32$; $A_r(Cl) = 35.5$; $A_r(Fe) = 56$; $A_r(Cu) = 64$

PASSAGE II

A sample of 2.3793 g of crystallohydrate of the type $M_xA_y.z\,H_2O$, where M is a metal was reacted with an excess of $SOCl_2$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $SOCl_2$ carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulphur.

In another experiment, 1.1896 g of the initial substance were dissolved in water and the solution was diluted to a volume of 100 cm^3. One fifth of this solution was required to react with 10 cm^3 of a 0.2-molar $AgNO_3$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.) ($M_{BaSO_4} = 233.4$)

3. Calculate the molecular formula of the crystallohydrate.
4. If you know that the sample can contain a maximum of seven moles of water per one mole of the crystallohydrate, give an example of another possible hydrate that cannot come into consideration due to the given limitation.

PASSAGE III

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:

I. $2\,MnO_4^- + 1H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 3O_2 + 4H_2O$

II. $2\,MnO_4^- + 3H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 4O_2 + 6H_2O$

III. $2\,MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

IV. $2\,MnO_4^- + 7H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 6O_2 + 10H_2O$

5. The correct possible ratios of the reactants in the above equations is expressed by:

   (*a*) I (*b*) II (*c*) III (*d*) IV

6. How much potassium permanganate (in mg) is needed to release 112 cm^3 of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

PASSAGE IV

Chromium exists as $FeCr_2O_4$ in the nature and it contains $Fe_{0.95}O$ & other impurity. To obtain pure chromium from $FeCr_2O_4$, the ore is fused with KOH and oxygen is passed through the mixture when K_2CrO_4 and Fe_2O_3 are produced.

$$FeCr_2O_4 + KOH + O_2 \longrightarrow K_2CrO_4 + Fe_2O_3$$

$$Fe_{0.95}O + O_2 \longrightarrow Fe_2O_3$$

2 g of ore required 280 mL of O_2 at 273 K and 1 atm for complete oxidation of ore. K_2CrO_4 is precipitated as $BaCrO_4$ when Barium salt is added. To remaining solution 10 mL of 1 M $K_4Fe(CN)_6$ is added when Fe^{3+} ions react with it to form $KFe[Fe(CN)_6]$, often called 'Prussian Blue'. To determine excess of $K_4Fe(CN)_6$ in solution, 7mL of 0.2 N of Fe^{2+} is added when all the $K_4Fe(CN)_6$ is precipitated as $K_2Fe[Fe(CN)_6]$.

7. What % of total iron present in $Fe_{0.95}O$ is in +2 state?

   (*a*) 99.64 (*b*) 85.29 (*c*) 65.82 (*d*) 89.47

8. % by mass of $Fe_{0.95}O$ in the ore is ____

   (*a*) 9.6% (*b*) 10.1% (*c*) 8.55% (*d*) 20.2%

9. n factor for $Fe_{0.95}O$ is ____

   (*a*) 0.9 (*b*) 0.85 (*c*) $\frac{2}{0.95}$ (*d*) 1.8

INTEGER TYPE QUESTIONS

10. Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:

    $$CH_3CH(NH_2)COOH + HNO_2 \rightarrow CH_3CH(OH)COOH + N_2 + H_2O$$

    Another method consists of the reaction of amino acids with a volumetric solution of perchloric acid, for example:

    $$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(N^+H_3)COOH + ClO_4^-$$

    The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

    50.0 cm^3 of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 cm^3.

    What would be the volume (in cm^3) of the nitrogen released at a pressure of 102.658 kPa and a temperature of 20°C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

ANSWER KEY

CONCEPT APPLICATION

1. (*a*) **2.** (*d*) **3.** (*a*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*a*) **8.** (*a*) **9.** (*c*)

SCHOOL LEVEL PROBLEMS

1. (*c*) **2.** (*a*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*a*) **8.** (*a*) **9.** (*a*) **10.** (*a*)
11. (*d*) **12.** (*a*) **24.** (i)-(*b*), (ii)-(*c*), (iii)-(*c*), (iv)-(*d*)

PRARAMBH (TOPICWISE)

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*a*) **8.** (*b*) **9.** (*a*) **10.** (*d*)
11. (*a*) **12.** (*b*) **13.** (*c*) **14.** (*a*) **15.** (*c*) **16.** (*d*) **17.** (*c*) **18.** (*a*) **19.** (*a*) **20.** (*d*)
21. (*a*) **22.** (*d*) **23.** (*d*) **24.** (*c*) **25.** (*a*) **26.** (*a*) **27.** (*c*) **28.** (*d*) **29.** (*d*) **30.** (*b*)
31. (*a*) **32.** (*d*) **33.** (*b*) **34.** (*a*) **35.** (*a*) **36.** (*c*) **37.** (*c*) **38.** (*c*) **39.** (*c*) **40.** (*d*)
41. (*a*) **42.** (*d*) **43.** (*b*) **44.** (*c*) **45.** (*a*)

PRABAL (JEE MAIN LEVEL)

1. (*d*) **2.** (*c*) **3.** (*d*) **4.** (*c*) **5.** (*a*) **6.** (*c*) **7.** (*c*) **8.** (*b*) **9.** (*b*) **10.** (*c*)
11. (*c*) **12.** (*b*) **13.** (*a*) **14.** (*a*) **15.** (*b*) **16.** (*c*) **17.** (*c*) **18.** (*a*) **19.** (*a*) **20.** (*a*)
21. (*a*) **22.** (*a*) **23.** (*d*) **24.** (*d*) **25.** (*a*) **26.** (*a*) **27.** (*c*) **28.** (*a*) **29.** (*b*) **30.** (*c*)
31. (*a*) **32.** (*a*) **33.** (*a*) **34.** (*a*) **35.** (*a*) **36.** (*c*) **37.** (*d*) **38.** (*d*) **39.** (*c*) **40.** (*c*)
41. (*c*) **42.** [2] **43.** [6] **44.** [1] **45.** [3] **46.** [3] **47.** [66] **48.** [6]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*b*) **2.** (*d*) **3.** (*b*) **4.** (*a*) **5.** (*c*) **6.** (*c*) **7.** (*a*) **8.** (*c*) **9.** (*c*) **10.** (*b*)
11. (*c*) **12.** (*d*) **13.** (*a*) **14.** (*a*) **15.** (*c*) **16.** (*b*) **17.** (*b*) **18.** (*b,c*) **19.** (*a,b,c*) **20.** (*a,b*)
21. (*a,c*) **22.** (*a,b,c,d*) **23.** (*a,c*) **24.** (*a,c,d*) **25.** (*a,b,d*) **26.** (*a,c,d*) **27.** (*a,b,d*) **28.** (*a,d*) **29.** (*c*) **30.** (*a*)
31. (*b*) **32.** (*b*) **33.** (*c*) **34.** (*d*) **35.** (*c*) **36.** (*a*) **37.** (*a*) **38.** (*a*) **39.** (*a*) **40.** [80]
41. [80] **42.** [27] **43.** [3] **44.** [7] **45.** [121] **46.** [75] **47.** [90] **48.** [1150] **49.** [190] **50.** [38]
51. [6] **52.** [448] **53.** [24.8] **54.** [5.08]

PYQ's (PAST YEAR QUESTIONS)

1. [3] **2.** (*a*) **3.** (*c*) **4.** [6] **5.** [59] **6.** [6] **7.** (*d*) **8.** [0] **9.** [1] **10.** (*c*)
11. (*b*) **12.** (*c*) **13.** (*b*) **14.** [6] **15.** (*a*) **16.** [6] **17.** (*a*) **18.** (*d*) **19.** (*d*) **20.** (*d*)
21. (*a*) **22.** (*a*) **23.** (*c*) **24.** (*d*) **25.** (*d*) **26.** [12] **27.** (*c*) **28.** [19] **29.** (*c*) **30.** [4]
31. (*a*) **32.** [8] **33.** (*d*) **34.** [2] **35.** (*d*) **36.** [1] **37.** (*a*) **38.** [24] **39.** [173] **40.** [50]
41. [18] **42.** [1575] **43.** [525] **44.** [24] **45.** (*b*) **46.** (*a*)

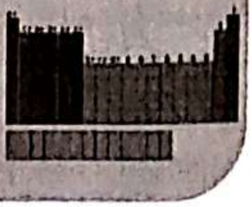
PW CHALLENGERS

1. [68] **2.** [448] **3.** $[CoCl_2.6H_2O]$ **4.** $[YCl_3.9H_2O]$ **5.** (*c*) **6.** [316] **7.** (*d*) **8.** (*b*)
9. (*b*) **10.** [617]

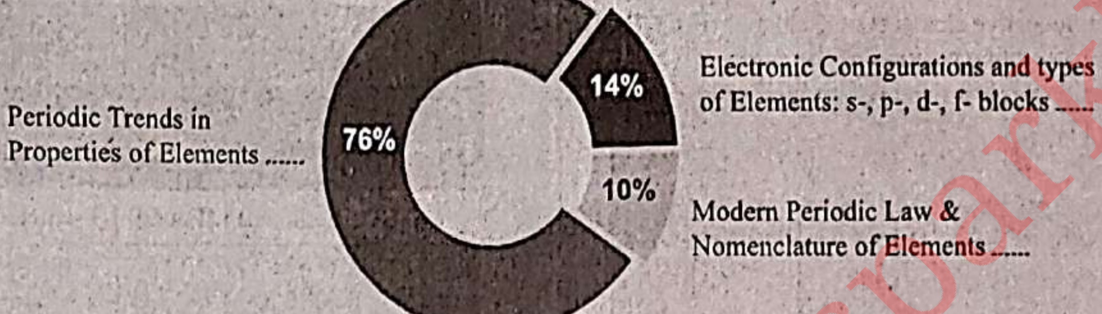
CHAPTER

4

Classification of Elements and Periodicity in Properties



Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

INTRODUCTION

The periodic table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the periodic table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements.**Glenn T. Seaborg**

NEED FOR CLASSIFICATION OF ELEMENTS

With the advent of time, chemistry had come a long way of development. Till date a large number of elements had been discovered which is quite remarkable from 31 elements in 1800 to 118 till date. Out of these 94 elements are naturally occurring and rest are man-made. While efforts to synthesize new elements are still going, it becomes a difficult task to study each and every element precisely and their compounds. So an appreciable amount of attention is required to systematise and arrange in a manner according to their properties. This will not only rationalize the known chemical facts about elements but will also leave scope for the predicted elements.

HISTORICAL DEVELOPMENT OF PERIODIC TABLE

Dobereiner's Law of Triads

The German scientist, **Johann Dobereiner** in early 1800's was the first to consider the idea of trends among properties of elements. By 1829, he gave his law of triads about **a group of three elements possessing similar characteristics, the atomic mass of the central element was nearly the arithmetic mean of the atomic masses of the other two elements (see table). The properties of the middle element were also in between those of the other two members.**

Table: Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Drawback: The concept was not applicable to all known elements but only to a limited number of elements.

Newland's Law of Octaves

An English chemist, **John Alexander Newlands** in 1865 made an attempt to classify the elements known in the increasing order of their atomic masses. He noticed that **every eighth element of the series has properties similar to the first element as every note resembles the first in octave of music.** It means that after a difference of seven elements, the element with similar characteristics was observed.

Table: Newland's Octaves

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Na	23	K	39
Be	9	Mg	24	Ca	40
B	11	Al	27		
C	12	Si	29		
N	14	P	31		
O	16	S	32		
F	19	Cl	35.5		

Drawback: The system worked only for lighter elements upto Calcium.

[illegible] Curve [1869]

He plotted a curve between atomic weight and atomic volume of different elements.

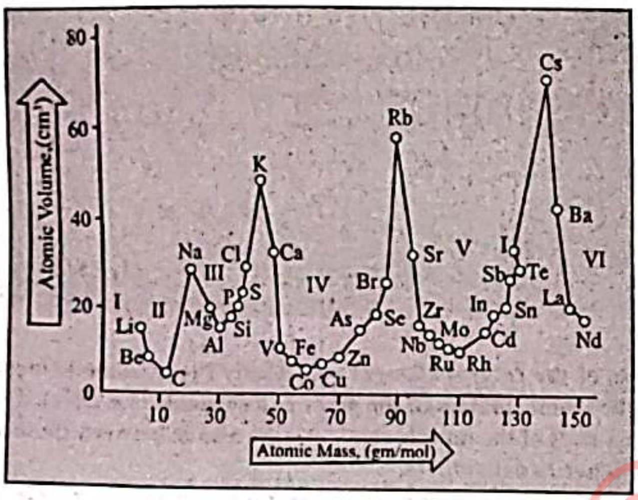
Elements having similar properties occupy similar positions on curve. The following observation can be made from the curve –

(*a*) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak positions on the curve.

(*b*) Less electropositive i.e. alkaline earth metal (Be, Mg, Ca, Sr, Ba) occupy the descending position on the curve.

(*c*) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.

(*d*) Most electronegative elements i.e. halogens (F, Cl, Br, I) occupy the ascending position on the curve.



Mendeleev's Periodic Table

The physical and chemical properties of elements are the periodic function of their atomic weights.

Characteristic of Mendeleev's Periodic Table

(*a*) 63 elements were known, noble gases were not discovered.

(*b*) He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.

(*c*) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.

(*d*) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.

(*e*) Each group upto VII is divided into A & B subgroups.'A' sub group elements are called normal elements and 'B' sub group elements are called transition elements.

(*f*) The VIII group consists of 9 elements in three rows.

(*g*) The elements belonging to same group exhibit similar properties.

Table: System of the Elements in Groups and Series

Merits or Advantages of Mendeleev's Periodic Table

(*a*) **Study of elements –** For the first time, all known elements were classified in groups according to their similar properties. So study of the properties of elements became easier.

(*b*) **Prediction of new elements –** It gave encouragement to the discovery of new elements as some gaps were left in it.

The primary aim of Mendeleev was to arrange elements with similar properties in the same group and predicted about some elements that were still undiscovered. He left a number of gaps for those unknown elements. Gallium and Germanium were not known when Mendeleev presented his periodic table. These elements were named Eka-Aluminium and Eka-Silicon. Mendeleev not only predicted about the existence of Gallium and Germanium but their properties actually matched the properties when these elements were discovered.

Table: Mendeleev's Predictions for the Elements Eka-Aluminium (Gallium) and Eka-Silicon (Germanium)

Property	Eka-aluminium	Gallium	Eka-silicon	Germanium
	(Predicted)	(Found)	(Predicted)	(Found)
Atomic weight	68	70	72	72.6
Density/ (g/cm³)	5.9	5.94	5.5	5.36
Melting point/(K)	Low	303K	High	1218K
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

For following elements, position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

Eka aluminium – Gallium (Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

(*c*) **Correction of doubtful atomic weights –** Corrections were done in atomic weight of some elements.

Atomic Weight = Valency × Equivalent weight.

Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent (V = 3), so the atomic weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent (V = 2). So, the atomic weight of Be became 2 × 4.5 = 9 and there was a space between Li and B for this element in Mendeleev's table.

Corrections were done in atomic weight of some other elements also – U, In, Au, Pt.

SERIES	GROUPS OF ELEMENTS										
	0	I	II	III	IV	V	VI	VII	VIII		
1	-	Hydrogen H 1.008									
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0			
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45			
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9	Cobalt Co 59	Nickel Ni 59
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95			
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Ru 101.7	Rhodium Rh 103.0	Palladium Pd (Ag) 106.5
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9			
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-			
9		-	-	-	-	-	-	-			
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Os 191	Iridium Ir 193	Platinum Pt 194.9
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-			
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239				
					HIGHER SALINE OXIDES						
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
					HIGHER GASEOUS HYDROGEN COMPOUNDS						
					RH_4	RH_3	RH_2	RH			

Demerits of Mendeleev's Periodic Table

(*a*) **Position of hydrogen:** Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties, so Mendeleev could not decide where to place it.

(*b*) **Position of isotopes:** As atomic wt. of isotopes differ, they should have been placed in different positions in Mendeleev's periodic table. But there were no such places for isotopes in Mendeleev's table.

(*c*) **Anomalous pairs of elements:** There were some pair of elements which didn't follow the increasing order of atomic weights.

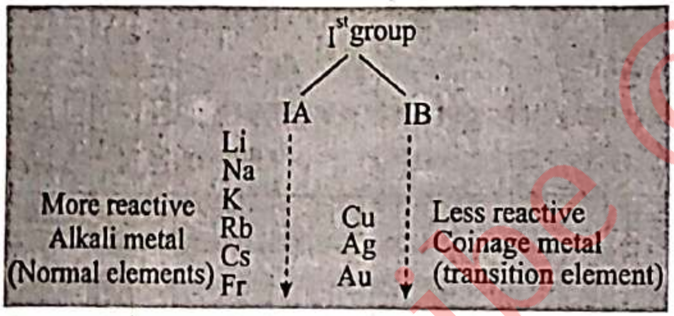
Ex. Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

(*d*) **Like elements were placed in different groups:**

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev's Periodic table.

Pt	Au
VIII	IB

(*e*) **Unlike elements were placed in same group:**



(*f*) It was not clear that **'lanthanides and Actinides'** are related with IIIA group or IIIB group.

MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

After development of atomic structure theories about sub-atomic particles, some spectacular achievements took place into the classification of elements. In 1913, the English physicist, **Henry Moseley** observed regularities in the characteristic X-ray spectra of the elements where he found that a plot of $\sqrt{v}$ (where v is frequency of k_α X-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{v}$ against atomic mass. Thus he concluded that the atomic number is more fundamental property than atomic mass. So he modified Mendeleev's periodic table and defined the modern periodic law as **"The physical and chemical properties of the elements are periodic functions of their atomic numbers".**

The periodic law revealed important characteristics among the 94 naturally occurring elements.

Modern Periodic Table

Various tables devised from time to time could not stand to the simplicity and informative modern form of periodic table known as **"long form"** of the periodic table of the elements. It was based on **Bohr-Bury concept** of electronic configuration.

Salient Features of the Modern Periodic Table

(*a*) It contains 7 horizontal rows like that of Mendeleev series called periods and 18 vertical columns called groups.

(*b*) Elements with similar valence shell configuration are arranged in same group.

(*c*) Each period corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18, 32 and 32 elements respectively.

(*d*) Fourteen elements of both sixth and seventh periods /i.e., **lanthanoids** and **actinoids** respectively are placed in separate panels at the bottom

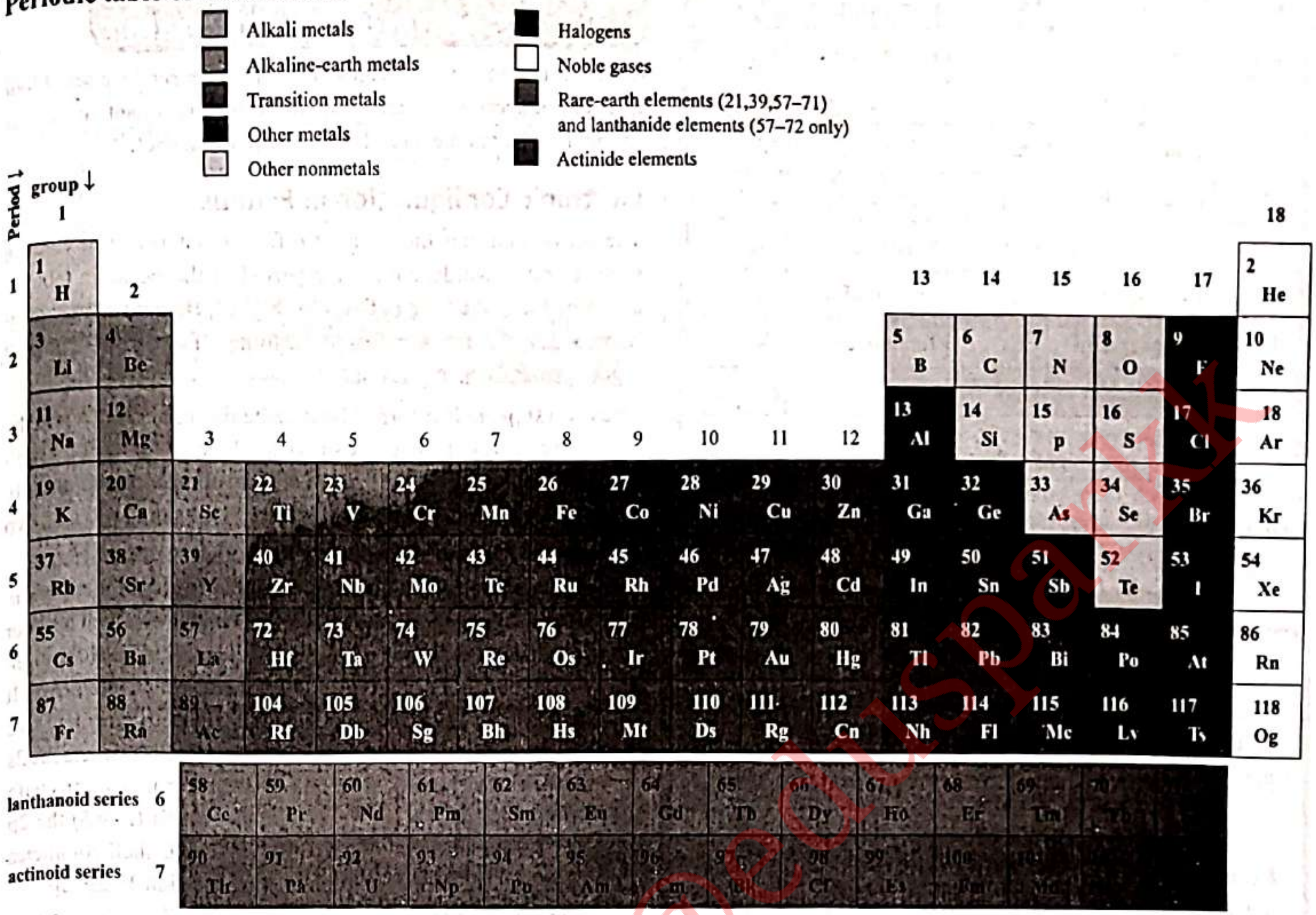
Merits of long form of Periodic Table over Mendeleev's Periodic Table

- **Positions of Isotopes and Isobars:** Isotopes have same atomic number and the periodic table is based on atomic numbers. Therefore, various isotopes of the same elements have to be provided the same position in the periodic table. Isobars have same atomic weights but different atomic numbers and therefore they have to be placed at different positions.
- The general electronic configuration of the elements remains same in group.

Defects of Long Form of Periodic Table

- The position of hydrogen is still disputable as it was there in Mendeleev's periodic table.
- Helium is an inert gas but its configuration is different from that of the other inert gas elements
- Lanthanide and actinide series could not be adjusted in the main periodic table and therefore they had to be placed in a separate block below the periodic table.
- Isotopes have different physical properties, but all isotopes of an element are provided with same position.

Periodic table of the elements



▨ Alkali metals
▨ Alkaline-earth metals
■ Transition metals
■ Other metals
□ Other nonmetals
■ Halogens
□ Noble gases
■ Rare-earth elements (21,39,57–71) and lanthanide elements (57–72 only)
■ Actinide elements

Period ↓ group ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

New elements with very high atomic numbers are very unstable that they can be obtained in very small quantities. Discovering new elements requires sophisticated technologies which is possessed by few countries only. Scientists are tempted to claim for its discovery which may lead to dispute between these countries due to competitive spirits.

For example, both American and Soviet scientists claimed credit for discovering element **104**. The Americans named it **Rutherfordium,** whereas Soviets named it **Kurchatovium.**

So, to avoid such problems IUPAC has given recommendation that until a new discovery is proved and its name is officially recognized, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1 – 9. The roots are put together in order of digits which make the atomic number and "ium" is added at the end.

Table: Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table: Nomenclature of Elements with Atomic Number above 100

Atomic Number	Name	Symbol	IUPAC Official Name	IUPAC symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt

110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

The permanent name might reflect the country (or state of the country) in which the element was discovered, or tribute to a notable scientist.

Train Your Brain

Example 1: What would be the IUPAC name and symbol for the element with atomic number 120?

Sol. The root for 1, 2 and 0 are un, bi and nil respectively. Hence, the name becomes unbinilium and the symbol is Ubn.

Example 2: What is the atomic number of Ununhexium?

Sol. Un – 1
Un – 1
Hex – 6

Concept Application

1. In modern periodic table, the element with atomic number Z = 118 will be:
   (*a*) Uuo ; Ununoctium ; alkaline earth metal
   (*b*) Uno ; Unniloctium ; transition metal
   (*c*) Uno ; Unniloctium; alkali metal
   (*d*) Uuo ; Ununoctium; noble gas
2. Unnilbium belongs to which block and group of the periodic table?
   (*a*) d-block, group-10 (*b*) f-block, group-3
   (*c*) p-block, group-13 (*d*) d-block, group-11
3. Atomic number of the recently discovered element Nihonium (Nh) is?
   (*a*) 118 (*b*) 114 (*c*) 113 (*d*) 104

ELECTRONIC CONFIGURATION OF ELEMENTS AND THE PERIODIC TABLE

We know that an electron in an atom is characterised by a set of four quantum numbers (n, *l*, m and s) where the principal quantum number (n) defines the main energy level known as the shell.

Electronic Configuration in Periods

The period indicates the value of **n** for the outermost or valence shell. In other words, successive period in the periodic table is associated with the filling of the next higher principal energy level like n = 1, n = 2, n = 3 refers to the filling of the 1st, 2nd, 3rd and higher principal energy levels.

(*a*) **First period:** It corresponds to the filling of electrons in the first energy shell i.e., (K shell), n = 1, since this energy shell has only one orbital, i.e. 1s which can accommodate only two electrons, therefore the first period contains only two elements. Hydrogen ($1s^1$) and Helium ($1s^2$).

(*b*) **Second period:** It corresponds to the filling of electrons in the 2nd energy shell (L shell) i.e. n = 2. Since this shell has four orbitals (one 2s and three 2p) which can accommodate eight electrons therefore 2nd period contains eight elements. It starts with Li (Z = 3) which has three electrons where two electrons are in the 1s orbital and third electron enters the 2s orbital. The next element Be (Z = 4) has four electrons with configuration $1s^22s^2$. From next element B (Z = 5) the 2p orbitals are filled with electrons and the L shell completes at Ne (Z = 10) with electronic configuration $1s^22s^2\ 2p^6$.

(*c*) **Third period:** This period corresponds to the filling of electrons in the third shell i.e., n = 3. This shell has nine orbitals (one 3s, three 3p and five 3d). However according to the energy level diagram of multielectron atoms, 3d-orbitals have high energy so they are filled after 4s-orbital. Consequently the third period contains only four orbitals (3s and 3p) accommodating only eight electrons. Thus 3rd period has only eight elements. It begins at sodium (Z = 11) where the added electron enters the 3s orbital. Successive filling of electrons completing the 3s and 3p orbitals ends at Argon (Z = 18) with electronic configuration $3s^23p^6$.

(*d*) **Fourth period:** It corresponds to the filling of electrons in the fourth energy level i.e., n = 4. It starts with potassium (Z = 19) and the added electron first goes to 4s-orbital which completes at calcium (Z = 20). After filling of 4s orbital, filling of five 3d-orbital starts that can accommodate ten electrons (before the filling of 4p-orbital, first filling of 3d orbitals take place). In the fourth period there are nine orbitals in total which can accommodate eighteen electrons i.e., eighteen elements.

(*e*) **Fifth period:** Fifth period corresponds to the fifth shell i.e., n = 5. Like fourth period it also have nine orbitals (one 5s, three 5p and five 4d) which can accommodate eighteen electrons i.e., it can have eighteen elements.

(*f*) **Sixth period:** It corresponds to the filling of the sixth energy level i.e., n = 6. Since in this period only sixteen orbitals (one 6s, seven 4f, five 5d and three 6p) are available, thereby sixth period contains thirty two elements.

(*g*) **Seventh period:** It corresponds to the filling of the seventh energy shell, i.e., n = 7. Like sixth period, it also contains thirty two elements due to the sixteen orbitals (one 7s, seven 5f, five 6d and three 7p). This includes most of the man-made radioactive elements.

METHOD TO PREDICT THE PERIOD, GROUP AND BLOCK OF A GIVEN ELEMENT

Following steps are followed to predict the group, period and block of the element:

1. Electronic configuration of the element is written by following various rules (Afbau principle, Hund's rule etc.).
2. Period of the element is represented by the highest principal quantum number of the valence shell.
3. Block of the element is predicted on the basis of sub-shell which receives the last electron.
4. Group is predicted from the number of electrons in the outermost or penultimate shell as follows:
   (*a*) In case the element belongs to s-block, then the group no. = (number of valence "s" electrons)
   (*b*) In case the element belongs to p-block, then the group no. = (10 + total number of valence "s" and "p" electrons)
   (*c*) In case the element belongs to d-block, then the group no. = (number of electrons in (n - 1) d-subshell + n s-subshell).

Key Note

Maximum number of elements in period can be calculated by the following formula:

$$= \frac{(n+1)^2}{2}, \text{ for odd period, } n = 1,3,5,7,9.......$$

$$= \frac{(n+2)^2}{2}, \text{ for even period, } n = 2,4,6,8.......$$

Train Your Brain

Example 3: How would you justify the presence of 18 elements in the 5th period of the periodic table?

Sol. When n = 5, l = 0, 1, 2, 3, 4. The order of the increasing energy of orbitals are 5s < 4d < 5p. The total number of orbitals available are nine. The maximum number of electrons that can accommodate is 18 and therefore 18 elements are there in the 5th period.

Concept Application

4. Total no. of elements which should be theoretically present in 8th period of the modern long form of periodic table, is:

   (*a*) 32 (*b*) 40 (*c*) 50 (*d*) 48

5. Atomic number Z = 58 belongs to which period, block and group

   (*a*) 4th period, d-block and 3rd group
   (*b*) 6th period, d-block and 4th group
   (*c*) 6th period, f-block and 3rd group
   (*d*) 5th, d-block and 5th group

CLASSIFICATION OF ELEMENTS ON THE BASIS OF ELECTRONIC CONFIGURATION

On the basis of electronic configuration, the elements can be classified into the following **four** blocks.

(*i*) **s-block elements :** Those elements in which last electron enters in s-orbital, are called s-block elements. These elements contain 1 or 2 electrons in s-subshell of outermost shell. Elements of 1st and 2nd group belong to this class. These elements enter into chemical reaction by losing valence electrons so as to acquire noble gas configuration in the outermost orbit.

ns^1 (group 1)	ns^2 (group 2)
(Alkali metals)	(Alkaline earth metals)

These elements generally form electrovalent compounds and basic oxides.

(*ii*) **p-block elements:** These elements contain 1 to 6 electrons in the p-subshell of the outermost orbit ($ns^2\ np^{1-6}$). The elements belonging to 13th to 18th group are p-block elements. In these last electron enters in p-subshell. For example:

Group	Elements	At.No.	Configuration
13	Boron (B)	Z = 5	$1s^2\ 2s^2\ 2p^1$
14	Carbon (C)	Z = 6	$1s^2\ 2s^2\ 2p^2$
15	Nitrogen (N)	Z = 7	$1s^2\ 2s^2\ 2p^3$
16	Oxygen (O)	Z = 8	$1s^2\ 2s^2\ 2p^4$
17	Fluorine (F)	Z = 9	$1s^2\ 2s^2\ 2p^5$

Note: 15, 16 and 17 group elements are called pnictogens, chalcogens and halogens respectively.

The main characteristics of these elements are:

(*a*) The non - metallic character increases along a period from group 13 to 17.

(*b*) They form covalent compounds among themselves but electrovalent (ionic) compounds with s-block elements.

(*iii*) **d-block elements :** Those elements in which last electron enters in d-orbital, are called d-block elements. These are also called transition elements. The elements of group 3 to 12 belong to this class. Their general configuration can be represented as : $(n-1)d^{1-10}\ ns^{1-2}$

General characteristics of transition (d-block) elements are:

- (*a*) These are metals, hard, malleable, ductile and possess high tensile strength.
- (*b*) These are good conductors of heat and electricity.
- (*c*) These elements exhibit variable valency.
- (*d*) These generally form coloured compounds.
- (*e*) These metals, their alloys and compounds possess marked catalytic activity.

Note: Zn, Cd, Hg and Cn are not considered as transition elements because these have fully filled d^{10} configuration in atomic as well as oxidation state.

(*iv*) **f-block elements:** They are inner transition or f-block elements. These elements are arranged in the two rows at the bottom of the periodic table. In the first row, these are 14 elements from atomic number 58 to 71 known as **Lanthanides or rare earth elements.** The second row of elements from atomic number 90 to 103, are known as **actinides**. Their general electronic configuration can be represented as

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

They show most of the properties similar to each other and also their properties are similar to 'd' block elements.

Key Note

(1) Representative or normal elements: The p-Block Elements and the s-Block Elements are called the representative Elements or Main Group Elements. These consist of some metals, all non metals and metalloid. These are the elements which are found in nature in abundance and are reactive in nature. These elements have one of the following configurations in their outermost shell.

ns^1, ns^2, ns^2np^1, ns^2np^2, ns^2np^3, ns^2np^4, ns^2np^5

The number of electrons in the outermost shell varies from 1 to 7

(2) Inert gases: At the end of each period is a noble gas element with a closed valence shell ns^2np^6 (exception helium having $1s^2$) configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Under special conditions, the higher members do form some compounds with other elements and hence, the name has been changed to Noble gases.

CLASSIFICATION OF ELEMENTS AS METALS, NON-METALS AND METALLOIDS

Though elements are classified into s, p, d and f-blocks, it is possible to further classify them into metals, non-metals and metalloids. More than 78% of the known elements are metals. These elements are present on the left side and centre of the periodic table. Metals are the elements which are malleable and ductile, possess lustre, are good conductors of heat and electricity and have high densities.

Metals usually have high melting points and boiling points and generally are solids at room temperature. Mercury is an exception which despite of being a metal is liquid at room temperature. **Gallium** (303 K) and **Caesium** (302 K) also have very low melting points. Non-metals are much less in number than metals.

There are only about 20 non-metals. These are located at the top right hand side of the periodic table. Non-metals have low melting points and low boiling points. They usually are solids or gases at room temperature. These non metals are neither ductile nor malleable. They are poor conductor of heat and electricity. In a period, the non-metallic character increases from left to right. Metallic character increases down the group.

There is no sharp line dividing metals from non-metals. A zig-zag line separates the metals from non-metals. The borderline elements such as silicon, germanium, arsenic, antimony and tellurium exhibit characteristic properties of metals as well as non-metals. These elements are called **semi-metals or metalloids.**

Train Your Brain

Example 4: Explain that Cu, Ag and Au are transition elements?

Sol. These elements are transition elements because these elements have incomplete (n–1)d subshell in their elemental state or in any stable oxidation state.

Example 5: Why 16th group elements are known as chalcogens?

Sol. 16th group elements are known as chalcogens or the ore-forming elements because many elements can be extracted from sulphide or oxide ores.

Example 6: How many of the given element(s) belongs to oxygen family?

Cd, Ba, Mo, Te, Ra, La, Po

Sol. Te, Po belongs to oxygen family.

Concept Application

6. What is the atomic number of the element which belongs to fifth period of 16th group?
   (*a*) 50 (*b*) 34 (*c*) 52 (*d*) 53
7. The group number for the inner transition elements is:
   (*a*) 3 (*b*) 6 (*c*) 4 (*d*) 8
8. Which is not d-block element?
   (*a*) Ag (*b*) Au (*c*) Pt (*d*) Yb
9. Which of the following is not a lanthanide element?
   (*a*) Samarium(Sm) (*b*) Terbium(Tb)
   (*c*) Holmium(Ho) (*d*) Einsteinium(Es)

SCREENING EFFECT (σ) AND EFFECTIVE NUCLEAR CHARGE (Z_{EFF})

(*i*) Valence shell e^- suffer force of attraction due to nucleus. and force of repulsion due to inner shell electrons.

(*ii*) The decrease in force of attraction on valence e^- due to inner shell e^- is called screening effect or shielding effect. (i.e. total repulsive force is called shielding effect.)

(*iii*) Due to screening effect, valence shell e^- experiences less force of attraction exerted by the nucleus. There is a reduction in nuclear charge on electron due to screening effect.

(*iv*) Reduced nuclear charge is called effective nuclear charge. Total net attraction force experienced by valence e^- is called Z_{eff}.

(*v*) If nuclear charge is Z, then effective nuclear charge is $(Z-\sigma)$
[Where σ (Sigma) = Screening constant]
So, $Z_{eff} = (Z-\sigma)$

Slater's Rule is used to determine Screening Constant (σ).

Slater's Rule

First write down the electronic configuration & then arrange in increasing order of shell.

eg $_{30}Zn = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

According to Slater,

$1s^2/2s^2 2p^6/3s^2 3p^6 3d^{10}/4s^2$

Rule-1: For s & p electrons

Remaining shell e^- of valence shell, shield by a factor of 0.35 & e^- in (n – 1) shell shield by a factor of 0.85 and remaining e^-s shield by a factor of 1.

screening constant for 4s electron,

$$_{30}Zn = \frac{1s^2/2s^2 2p^6}{(\times 1)}, \frac{3s^2 3p^6 3d^{10}}{(n-1)\times 0.85}, \frac{4s^2}{(n)\times 0.35}$$

$\sigma = 10 \times 1 + 18 \times 0.85 + 1 \times 0.35$

$\sigma = 25.65$

$Z_{eff} = Z - \sigma = 30 - 25.65 = 4.35$

Potassium ($Z = 19$) $= \underbrace{2,8}_{n-2}, \underbrace{8}_{n-1}, \underbrace{1}_{n}$

$Z_{eff} = Z - \sigma$

$$\left.\begin{aligned} Z_{eff} &= 19 - (10 \times 1 + 8 \times 0.85) \\ &= 19 - 16.8 = 2.2 \end{aligned}\right] \text{For valence } e^- \text{ of Potassium}$$

$$\left.\begin{aligned} &\textbf{Sodium } (Z = 11) = \underbrace{2}_{n-2}, \underbrace{8}_{n-1}, \underbrace{1}_{n} \\ &Z_{eff} = 11 - (2 \times 1 + 8 \times 0.85) \\ &\quad = 11 - 8.8 = 2.2 \end{aligned}\right] \text{For valence } e^- \text{ of sodium}$$

Rule-2: For d & f electrons

The remaining e^- in the same subshell (not shell) shield by factor of 0.35 & remaining e^- shield by a factor 1.

$$\left.\begin{aligned} \sigma_{3d}(Zn) &= 9 \times 0.35 + 18 \times 1 = 21.15 \\ Z_{eff} &= Z - \sigma = 30 - 21.15 = 8.85 \end{aligned}\right] \text{For 3d } e^- \text{ of zinc}$$

Key Note

Penetration effect:

Order of attraction of subshells towards nucleus (Penetration power) is: s > p > d > f, e.g., the penetration of a 2s-electron to the nucleus is more than that of a 2p-electron; hence the 2p electrons are more shielded from the nucleus by the inner core of electrons than 2s electrons.

PERIODICITY IN PROPERTIES

"The repetition of similar electronic configuration after a regular interval is the cause of periodicity of the properties of elements."

Cause of periodicity in properties of elements is due to repetition of similar outer electronic configurations after certain regular intervals. These regular intervals being 2, 8, 8, 18, 18 and 32. These numbers are also sometimes called as **magic number.**

Periodic properties are directly or indirectly related to their electronic configuration and show a regular gradation on moving from left to right in a period or from top to bottom in a group. Some important periodic properties are: **oxidation number, shielding effect, atomic radii, ionization energy, electron affinity, electro-negativity, valency, density, m.pt. and b.pt.**

ATOMIC RADII

Atom is considered to be a very small spherical entity. So, in simple terms atomic radii can be defined as the distance of the outermost shell of an atom from the centre of its nucleus. Being very small, it is usually expressed in nm

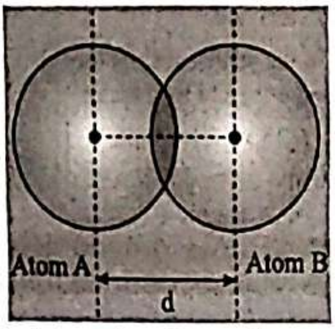
(1nm = 10Å = 10^3pm = 10^{-9}m).

Atomic radius is taken as the effective size which is the distance of closest approach of one atom to the another atom in a given bonded situation. Atomic radii can be measured by X-ray or other spectroscopic methods.

Various names had been proposed for the atomic radii depending upon their experimental determinations and nature of atom. These are:

(*i*) Covalent radius
(*ii*) Metallic radius
(*iii*) Ionic radius
(*iv*) Van der Waals radius

(*i*) **Covalent radius:** Covalent bond is normally formed between the non-metals hence this term, covalent radius is used for non-metals. It is defined as half of the internuclear distance between two successively covalently bonded atoms in a molecule.



Here d is the internuclear distance between two covalently bonded atoms A and B.

If we consider a covalently bonded chlorine molecule (Cl_2), the bond distance in it is 198 pm. The half of the distance (99 pm) is taken as the atomic radius of chlorine atom. The atomic radii of few elements are given below which gives an inference about the trends in the terms of nuclear charge and energy level.

Table: Atomic Radii/pm Across the period

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radius	186	160	143	117	110	104	99

Table: Atomic Radii/pm Down a Family

Atom (Group 1)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

If we observe the trend in atomic radii across the period and down the group, we find that the atomic size generally decreases across the period whereas there is an increase in the size down the group. The reason which can be attributed to this variation is the nuclear charge.

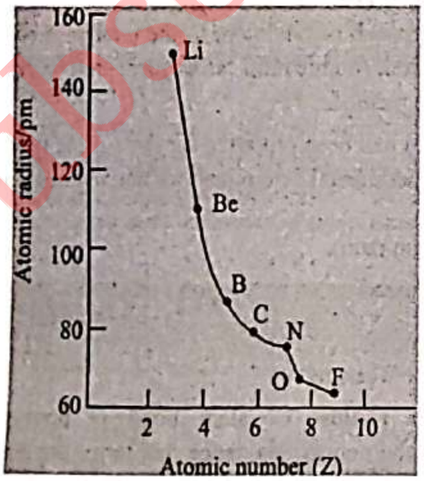


Fig. (*a*) Variation of atomic radius with atomic number across the second period

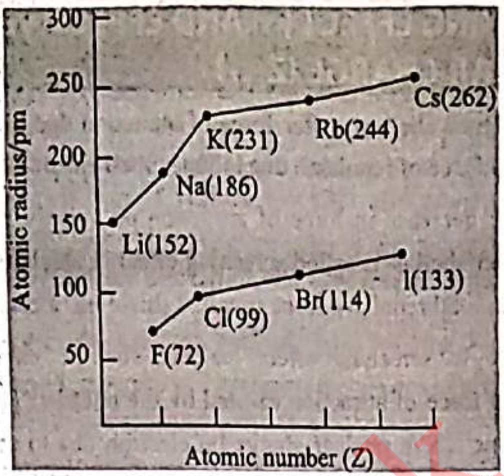


Fig. (*b*) Variation of atomic radius with atomic number for alkali metals and halogens

In a period as the atomic number increases, the increasing number of electrons are added to the same valence shell. This increases the effective nuclear charge, consequently the force of attraction of the electrons to the nucleus goes on increasing. Thus gradual increase in the effective nuclear charge results in the decrease of the atomic size along the period.

(*ii*) **Metallic radius:** Metallic radius is taken as half of the distance between two successive nuclei of two adjacent metal atoms in solid metal lattice.

For example, the distance between two adjacent copper atoms in solid copper is 256 pm hence, the metallic radius of copper is assigned a value of 128 pm.

(*iii*) **Ionic radius:** The removal of an electron from an atom results in the formation of a cation, whereas the gain of electron leads to the formation of an anion.

So, the ionic radius can be defined as the distance of outermost shell of an anion or cation from its nucleus. For example, the bond length (d_{A-B}) for an ionic solid is given as

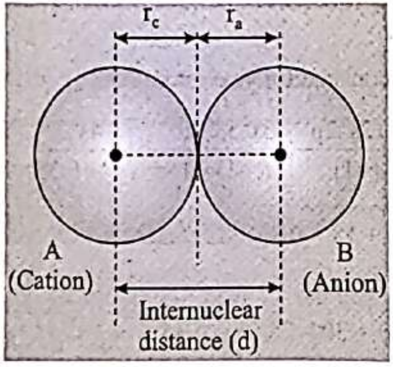
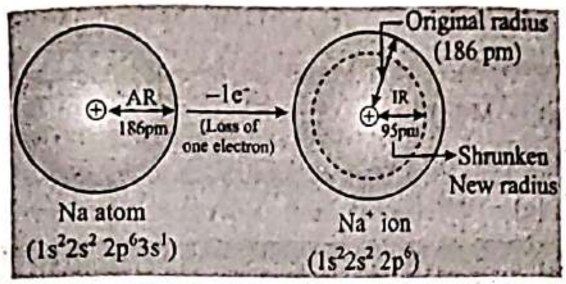


Fig. showing the bond length (d) between the cation and an anion of an ionic molecule AB.

$$d_{A-B} = r_C + r_A$$

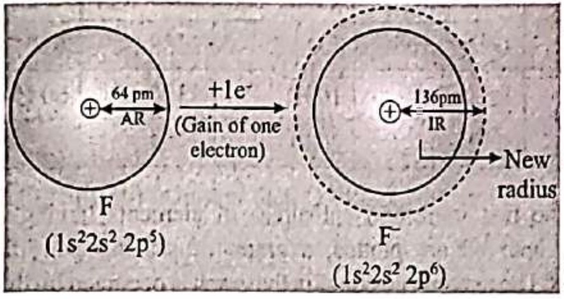
The size of a cation is always smaller than its parent atom because the cation formed after the loss of electron has fewer electrons. Though the nuclear charge remains the same, effective nuclear charge increases.

For example, the atomic radius of sodium is 186 pm whereas the ionic radius for sodium ion (Na^+) is 95 pm.



Atom	Li	Na	K	Rb	Cs
Atomic Radii (pm)	152	186	231	244	262
Ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic Radii (pm)	76	102	138	152	167

The size of the anion is always larger than the parent atom because addition of one or more electrons results in the increased repulsion among the electrons and a decreased effective nuclear charge. For example, the ionic radius of fluorine is 136 pm whereas the atomic radius is 64 pm.



Key Note

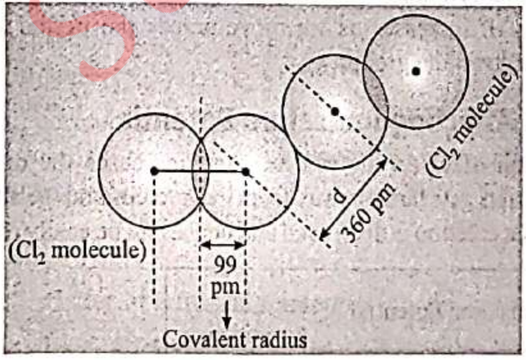
There are atoms and ions which contain the same number of electrons. These are known as **isoelectronic species.**

The cation with a greater positive charge has a smaller radius because of the greater nuclear attraction of the electrons while the anion with the greater negative charge has a larger radius.

Element	N	O	F	Na	Mg	Al
Atomic size (pm)	74	66	64	186	160	143
Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Ionic size (pm)	171	140	136	95	72	57

(*iv*) **Van der Waals radius:** It is defined as half the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules in solid state. This term is used for non-metals (in covalent compounds) and noble gases.

For example, the van der Waals radius of chlorine is 180 pm



van der Waals radius = $\frac{1}{2}$ × d (Internuclear distance between two non-bonded neighbouring atoms of two covalently bonded molecules)

$$\text{van der Waals radius of chlorine} = \frac{1}{2} \times 360$$

$$= 180 \text{ pm}$$

Note : Order of radius : covalent < metallic < van der Waals

PERIODIC VARIATION OF ATOMIC SIZE

(*i*) **Across a period:** It decreases from left to right in a period as nuclear charge increases

eg. Li > Be > B > C > N > O > F < Ne

(*ii*) **In a group:** It increases from top to bottom in a group as number of shell increases

eg. Li < Na < K < Rb < Cs

Exception : Transition elements

$$\underbrace{Sc > Ti > V > Cr}_{Z_{eff} > \text{Screening effect}} < Mn > \underbrace{Fe \approx Co \approx Ni}_{Z_{eff} \approx \text{Screening effect}} <$$

$$\underbrace{Cu < Zn}_{Z_{eff} < \text{Screening effect}}$$

Order of atomic radius –

Sc > Ti > V > Cr < Mn > Fe ≈ Co ≈ Ni < Cu < Zn

ADVANCED LEARNING

Lanthanoid Contraction

(*a*) Outermost electronic configuration of inner transition elements is
$(n-2)\, f^{1\text{-}14}\, (n-1)d^{0\text{-}1}\, ns^2$ (n = 6 or 7)

(*b*) Last e^- enters in (n – 2) f orbitals.

(*c*) Mutual screening effect of e^- is very less, because of complicated structure of f-orbital.

(*d*) Nuclear charge increases by one (+1) in lanthanides and actinides so atomic size of these elements slightly decreases. It is known as lanthanoid contraction.

(*e*) In Iˢᵗ, 2ⁿᵈ and 3ʳᵈ transition series,

Radii– 3d < 4d ≈ 5d **(except Gr. 13)**

	Gr. 3	Gr. 4	
size increases ↓	Sc	Ti	↓ size increases
	Y	Zr	
	La	Hf	} Equal size due to lanthanide contraction

Transition Contraction : Gr. 3 → B < Al ≈ Ga

Note: While atomic size should increase down the group.

(*a*) At. size of Ga < At. size of Al, due to transition contraction (d-contraction).

(*b*) In transition elements nuclear charge increases by 1. But last e^- enters in (n – 1)d orbital.

(*c*) Screening effect of (n – 1)d e^- balance the nuclear charge by 85%

(*d*) Z_{eff} increasing as on each electron = 1 – 0.85 = 0.15

(*e*) Increase in nuclear charge is only 0.15.

Different orders of atomic and ionic radii:

1. $Na^+ < Ne < F^-$
2. $Ni < Cu < Zn$
3. $H^+ < H < H^-$
4. $Ti < Zr \approx Hf$
5. $Be < Li < Na$
6. $Cr < V < Ti < Sc$
7. $I^+ < I < I^-$
8. $Sc < Y < La$
9. $Cl < Na < Ar$
10. $Cu < Au < Ag$

Train Your Brain

Example 7: On the basis of their positions in the periodic table which among the following will have the largest atomic radii?

Be, N, O, Ne

Sol. Ne has the largest size in its period. All the elements belong to the same period. (For noble gases van der Waal radii is considered)

Concept Application

10. What will be the distance between H and Cl atom in HCl (According to the concept of covalent radius)? If radius of hydrogen is 0.37 Å and the radius of chlorine is 1.67Å

(*a*) 2.04 Å
(*b*) 1.96 Å
(*c*) 2.12 Å
(*d*) 1.0 Å

11. Which of the following orders of atomic radii are correct?

(i) Li < Be < Na
(ii) Ni < Cu < Zn
(iii) Ti < Zr ≈ Hf
(iv) Ti > V > Cr

Correct code is:

(*a*) i, ii, iii, iv
(*b*) only ii
(*c*) ii, iii, iv
(*d*) only iv

IONIZATION ENTHALPY ($\Delta_i H°$)

It is also known as ionization potential or ionization energy which can be defined as the minimum amount of energy required to remove an electron from the valence shell of an isolated gaseous atom in its ground state resulting in the formation of positive ion.

$$M(g) \rightarrow M^+(g) + e^-$$

Since energy is always required to remove the electrons from the atom, ionization enthalpy is always positive.

The ionization enthalpy goes on increasing for each successive removal of electrons. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently the remaining electrons are held more tightly by the nucleus and removal of each successive electron becomes more difficult. Hence, successive ionization enthalpies go on increasing. So order becomes

$$IE_1 < IE_2 < IE_3 < ...$$

For example,

$$M(g) \rightarrow M^+(g) + e^-$$

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

Table: Successive ionization enthalpies (kJ/mol) of some elements

Element	Electronic configuration	IE_1 (kJ/mol)	IE_2 (kJ/mol)	IE_3 (kJ/mol)
Li	$1s^2 2s^1$	520	7297	11810
Be	$1s^2 2s^2$	899	1758	14810
B	$1s^2 2s^2 2p^1$	801	2428	3660
C	$1s^2 2s^2 2p^2$	1086	2353	4618
N	$1s^2 2s^2 2p^3$	1402	2855	4577
O	$1s^2 2s^2 2p^4$	1314	3388	5297
F	$1s^2 2s^2 2p^5$	1681	3375	6045
Ne	$1s^2 2s^2 2p^6$	2080	3963	6130

When the first ionization enthalpies of elements having atomic number upto 60 are plotted, a graph of striking periodicity is obtained. The maxima positions in the graph is occupied by the noble gases because of the high ionization enthalpies due to completely filled octet acquiring a stable electronic configuration. On the other hand, the alkali metals occupy the minima positions in the graph correlating the low ionization enthalpies and their high reactivity.

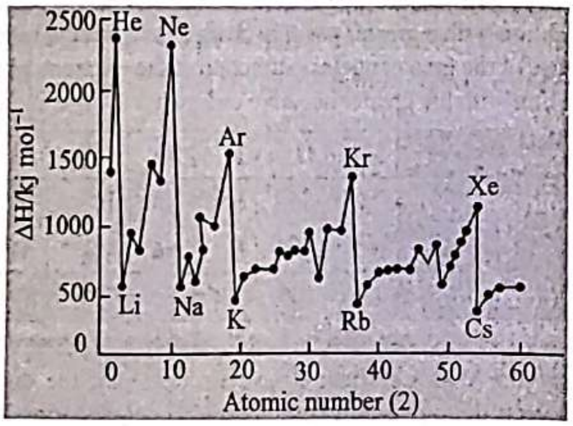


Fig. variation of first ionization enthalpies (ΔH) with atomic number for elements with Z = 1 to 60

Two noticeable trends are observed in respect to the first ionization enthalpies. It increases as we move across the period while it decreases down the group.

Factors Affecting Ionisation Potential

(*a*) **Atomic size:** As the size of atom increases the outermost electrons gets farther away from the nucleus and the attraction on that electron is decreased and hence can be easily removed.

$$\boxed{\text{Ionisation Potential} \propto \frac{1}{\text{Atomic size}}}$$

(b) Effective nuclear charge (Z_{eff}):

$$\boxed{\text{Ionisation Potential} \propto \text{Effective nuclear charge}}$$

(c) Penetration power of sub shells:

As s-subshell is more closer to nucleus so more energy will be required to remove e^- from s-subshell in comparison to p,d & f.

Ex. Be B

$1s^2 2s^2$ $1s^2 2s^2 2p^1$

first Ionisation Potential Be > B

After losing one e^-, B attains electronic configuration of Be; so IInd ionisation potential of B is more than Be. IInd Ionisation Potential of B > Be.

(d) Stability of half filled and fully filled orbitals:

(i) Half filled orbitals p^3, d^5, f^7 or fully filled orbitals s^2, p^6, d^{10}, f^{14} are more stable than others. So it is difficult to remove e^- from these configuration.

eg. N O

$1s^2\,2s^2\,2p^3$ $1s^2\,2s^2\,2p^4$

Ist Ionisation Potential order is O < N

Because of half filled p-orbitals in N, its ionisation energy (stability) is higher than O.

$$\boxed{\text{Also, I}^{st}\text{ ionisation potential order Na} < \text{Al} < \text{Mg}}$$

Because s-orbital in Mg is completely filled and its penetration power is also higher than p-orbital (Al).

IInd ionisation potential order: Mg < Al < Na.

I.E. order : $Mg^+ < Al^+ < Na^+$

(2,8,1) (2,8,2) (2,8)

(e) Oxidation state:

$$\boxed{\text{Ionisation Potential} \propto \text{oxidation state of an atom}}$$

Ion with high oxidation state will have high ionisation potential. **Ex.** $Fe^{3+} > Fe^{2+} > Fe$

PERIODIC VARIATION

(i) **In a group:** Size increase so ionisation potential decrease.

$$\xrightarrow{\text{Li} \quad \text{Na} \quad \text{K} \quad \text{Rb} \quad \text{Cs}}$$

Size increases, Ionisation Potential decreases

Exception:

- Ionisation Potential: Ga > Al is due to Transition contraction)
- Ionisation Potential $\left.\begin{array}{ccc} \text{Hf} & > & \text{Zr} \\ 5d & & 4d \end{array}\right\}$ (due to lanthanide contraction)

(ii) **In a period:** In a period atomic size decreases and Z_{eff} increases so removal of electron becomes difficult and ionisation potential increases.

$$\xrightarrow{\text{Li} \quad \text{Be} \quad \text{B} \quad \text{C} \quad \text{N} \quad \text{O} \quad \text{F} \quad \text{Ne}}$$

Order of ionisation potential

Li < B < Be < C < O < N < F < Ne

APPLICATION OF IONISATION POTENTIAL

(a) Metallic and non metallic character:

Metallic $\longrightarrow$ Low Ionisation Potential

(Na, K, Rb etc.)

Non metallic $\longrightarrow$ High Ionisation Potential

(F, Cl, Br etc.)

$$\boxed{\text{Ionisation Potential} \propto \frac{1}{\text{Metallic property}}}$$

(b) Reducing character:

$$\boxed{\text{Reducing character} \propto \frac{1}{\text{Ionisation Potential}}}$$

Group 1 elements has minimum ionisation potential in its period so they are strong reducing agents in gaseous state (Li < Na > K > Rb > Cs)

(c) Stability of oxidation states:

(i) If the difference between two successive ionisation potential ≥ 16eV then lower oxidation state is stable.

$$\text{eg. } \left.\begin{array}{l} \text{Na} \longrightarrow \text{Na}^+, \text{I}^{st} \text{ ionisation potential} \\ \text{Na}^+ \longrightarrow \text{Na}^{2+}, \text{II}^{nd} \text{ ionisation potential} \end{array}\right\} 42.7\text{ eV}$$

Difference of ionisation potential > 16 eV, so Na^+ is more stable.

(ii) If the difference between two successive ionisation potential ≤ 11 eV higher oxidation state is stable.

$$\text{eg. } \left.\begin{array}{l} \text{Mg} \longrightarrow \text{Mg}^+, \text{I}^{st} \text{ ionisation potential} \\ \text{Mg}^+ \longrightarrow \text{Mg}^{2+}, \text{II}^{nd} \text{ ionisation potential} \end{array}\right\} 7.4\text{ eV}$$

Difference of ionisation potential < 11 eV So Mg^{2+} is more stable.

$$\begin{array}{l} \left.\begin{array}{l} \text{Al} \longrightarrow \text{Al}^+ \\ \text{Al}^+ \longrightarrow \text{Al}^{2+} \end{array}\right\} 12.8\text{ eV so, Al}^+\text{ is more stable} \\ \left.\begin{array}{l} \text{Al}^+ \longrightarrow \text{Al}^{2+} \\ \text{Al}^{2+} \longrightarrow \text{Al}^{3+} \end{array}\right\} 6.0\text{ eV so, Al}^{3+}\text{ is more stable} \end{array}$$

$$\left\{\begin{array}{l} \text{Al}^+ \text{ is stable only in gaseous state} \\ \text{Al}^{3+} \text{ is stable in liquid and solid state.} \end{array}\right.$$

(d) Basic nature: It is property of elements with loosely held electrons

$$\boxed{\text{Ionisation Potential} \propto \frac{1}{\text{Basic Property}}}$$

$M_2O > MO \rightarrow Na_2O > MgO, NaOH > Mg(OH)_2$

$M_2O \rightarrow Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$

(e) To determine the number of valence electron:

Sudden change in values of IE indicate that next e^- is to be removed from inner shells.

eg. Li: Ist Ionisation Potential (5.4 e V) and IInd Ionisation Potential (75 eV)

High energy difference in two successive ionisation potential shows change in energy levels i.e., valence shell has only one electron.

Train Your Brain

Example 8: The first ionisation enthalpy values of 3rd period elements Na, Mg and Si are respectively 496, 737 and 786 kJ/mol. Predict whether the first ionisation enthalpy value for Aluminium will be more close to 575 or 760 kJ/mol justify your answer?

Sol. It will be more close to 575 kJ mol^{-1}. The IE value for Al should be lower than that of Mg.

Example 9: The first ionisation enthalpy values in kJ/mol of 13th group elements are:

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend.

Sol. Deviation from Al to Ga is due to poor shielding of d-electrons (Transition contraction) and deviation from In to Tl is due to that of Lanthanoid contraction.

Concept Application

12. In C, N, O, F which of the following orders is correct for Ionisation enthalpy?
    (*a*) F > O > C > N (*b*) O > F > N > C
    (*c*) F > N > O > C (*d*) N > F > O > C
13. Which of the following have highest difference in the value of IInd and IIIrd Ionisation enthalpy?
    (*a*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$ (*b*) $1s^2\,2s^2\,2p^6\,3s^2$
    (*c*) $1s^2\,2s^2\,2p^6\,3s^1$ (*d*) $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$
14. Which of the following has highest Ionisation enthalpy?
    (*a*) [Ne] $3s^2\,3p^1$ (*b*) [Ne] $3s^2\,3p^3$
    (*c*) [Ne] $3s^2\,3p^2$ (*d*) [Ar] $4s^2\,3d^{10}\,4p^3$

ELECTRON GAIN ENTHALPY/ELECTRON AFFINITY ($\Delta_{eg}H°$)

The amount of energy released when electron is added to the valence shell of an isolated gaseous atom is known as Electron affinity.

$$X + e^- \longrightarrow X^- + \text{Electron Affinity}$$

Mostly energy is released in the process of first Electron affinity.

$$X + e^- \longrightarrow X^- + \text{I}^{\text{st}}\ \text{Electron Affinity}$$

If Ist Electron affinity is exothermic, then

$\Delta_{eg}H$ (electron gain enthalpy) = – ve

Ist Electron addition is **mostly** positive

Electron affinity of neutral atom is equal to ionisation potential of its anion.

$$\text{eg. } X(g) + e^- \xrightleftharpoons[\text{Ionisation Potential}]{\text{Electron Affinity}} X^-(g) + \text{Energy}$$

On adding 2nd electron in anion X^-

$$X^- + e^- \longrightarrow X^{2-} + \text{II}^{\text{nd}}\ \text{Electron Affinity}$$

or

$$X^- + e^- + \text{II}^{\text{nd}}\ \text{Electron Affinity} \longrightarrow X^{2-},$$

$\Delta_{eg}H$ (2nd electron gain enthalpy) = + ve

IInd Electron affinity is endothermic process, i.e. energy has to be given to introduce 2nd electron in an anion, because of repulsion between negative charge on anion (X^-) and 2nd electron. Hence, IInd Electron Affinity is always negative.

eg. $O(g) + e^- \longrightarrow O^-(g) + 168$ K.cal/mol (exothermic)

$O^- + e^- \longrightarrow O^{2-} - 912.7$ K.cal/mol

Net reaction

$O(g) + 2e^- \longrightarrow O^{2-}(g)$

Total Electron Affinity = – 744.7 K.cal/mol (endothermic)

FACTORS AFFECTING ELECTRON AFFINITY

(*a*) Atomic size

$$\text{Electron Affinity} \propto \frac{1}{\text{Atomic size}}$$

(*b*) Screening effect

$$\text{Electron Affinity} \propto \frac{1}{\text{Screening effect}}$$

(*c*) Effective nuclear charge (Z_{eff})

Electron Affinity $\propto Z_{eff}$

(*d*) Stability of completely filled or half filled orbitals:

Electron affinity of completely filled or half filled orbital is very less or zero.

eg. (*i*) Elements (He, Ne, Ar, ...),
Electron Affinity = Zero

(*ii*) Elements (Be, Mg, Ca, ...),
Electron Affinity = Approximately Zero

(*iii*) Elements (N, P, As, ...),
Electron Affinity = Very less

PERIODIC VARIATION

In Period

(*a*) Electron affinity increases along the period due to increase in Z_{eff} and decrease in atomic size.

(*b*) Halogens possess maximum electron affinity due to small size and maximum Z_{eff} and after gaining one electron, they attain a stable inert gas configuration.

Li	$\boxed{Be}$	B	C	$\boxed{N}$	O	F	$\boxed{Ne}$
Na	$\boxed{Mg}$	Al	Si	$\boxed{P}$	S	Cl	$\boxed{Ar}$
	≈ zero			less			zero

In 2nd period – Ne < Be < N < B < C < O < F

In 3rd period – Ar < Mg < P < Al < Si < S < Cl

In Group

(*a*) Electron affinity decreases down the group. As the size increases and hence attraction on additional electron is decreased.

(*b*) Electron affinity values of 3rd period element are greater than electron affinity of 2nd period elements of the respective group.

F	Cl
$1s^2 2s^2 2p^5$	$[Ne]\ 3s^2 3p^5$

Due to small size of fluorine, **electron density around the nucleus increases.** The incoming electron suffers more repulsion.

Cl > F > Br > I	S > O > P > N
S > Se > O	Si > C > P > N

Key Note

Application of Electron Affinity

Electron affinity ∝ Oxidising nature

But F has more oxidising power than Cl because F

(*i*) Has high standard reduction potential.

(*ii*) Has high hydration enthalpy.

(*iii*) Low bond dissociation energy.

Train Your Brain

Example 10: Which of the following will have the most negative and which has the least negative values of electron gain enthalpy?

P, S, Cl, F.

Sol. Electron gain enthalpy generally become more negative across a period, as we move from left to right. Within the group electron gain enthalpy becomes less negative as we move down the group. However electron addition in 2p orbital lead to greater repulsion then the electron addition in 3p orbital. Hence, Chlorine has most negative EA and phosphorous has least negative EA.

Example 11: Arrange the following elements in increasing order of electron affinity.

F, Cl, O, N, B.

Sol. Cl > F > O > B > N → Nitrogen has stable electronic configuration

Concept Application

15. The process requiring the absorption of energy is -

(*a*) $F \rightarrow F^-$ (*b*) $Cl \rightarrow Cl^-$

(*c*) $O \rightarrow O^{2-}$ (*d*) $H \rightarrow H^-$

16. Arrange S, O and Se in ascending order of electron affinity

(*a*) Se < S < O (*b*) O < Se < S

(*c*) S < O < Se (*d*) S < Se < O

ELECTRONEGATIVITY

Electronegativity of an element is the tendency of an atom to attract the shared pair of electrons towards itself. It is a qualitative measure, because unlike ionization enthalpy and electron gain enthalpy which are related to atoms in the isolated gaseous state, it is in the bonded state and hence not a measurable quantity.

Although a number of numerical scales of electronegativity such as Pauling scale, Mulliken-Jaffe scale, Allred Rochow scale have been developed, Yet the Pauling scale is most widely used.

(*a*) Electronegativity values (on Pauling scale) Across the periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

(*b*) Electronegativity values (on Pauling scale) Down a group

Atom (Group 1)	Electronegativity value	Atom (Group 17)	Electronegativity value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

The electronegativity of any given element is not constant, it varies depending on its hybridisation and the element to which it is bonded. Even though it is a qualitative quantity, it helps in the prediction of the type of bond which exists between two bonded atoms.

FORMULA TO DETERMINE ELECTRONEGATIVITY

(*i*) **Mulliken scale:**

$$\text{Electronegativity} = \frac{IE_1 + EA_1}{2}$$

(*ii*) **Pauling scale:**

$$\text{Electronegativity} = \frac{\text{Mulliken scale}}{2.8}$$

(*iii*) **Allred Roschow's Scale:**

As per Roschow, electronegativity is the force by which nucleus of an atom attracts electron.

$$\boxed{(X_{AR})\ \text{Electronegativity} = \frac{0.359\,Z_{eff}}{r^2}}$$

r is the covalent radius in Å and Z_{eff} is the effective nuclear charge on incoming electron.

Note: $\boxed{X_P = X_{AR} + 0.744}$

FACTORS AFFECTING ELECTRONEGATIVITY

(*a*) **Atomic size**

$$\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}$$

(*b*) **Effective nuclear charge (Z_{eff})**

Electronegativity $\propto Z_{eff}$

(*c*) **Hybridisation state of an atom**

Electronegativity $\propto$ % s character in hybridised atom

	sp >	sp^2 >	sp^3
s character	50%	33%	25%
Electronegativity of carbon	3.25	2.75	2.5

(*d*) **Oxidation state**

Electronegativity $\propto$ oxidation state e.g.

(i) $Mn^{2+} < Mn^{4+} < Mn^{7+}$

(ii) $O^{2-} < O^{-} < O < O^{+} < O^{2+}$

(iii) $Fe < Fe^{2+} < Fe^{3+}$

Periodic Table & Electronegativity

(*a*) Electronegativity decreases down the group.

(*b*) In period on moving from left to right, electronegativity increases.

Exceptions: In group 18 – Electronegativity is zero, because inert gases do not form molecule.

(*c*) Electronegativity of Cs and Fr are equal, it is because from $_{55}Cs$ to $_{87}Fr$ only one shell increases but nuclear charge (No. of proton) increases by +32.

So effect of nuclear charge balanced the effect of increase in number of shell.

(*d*) Electronegativity of F > Cl but Electron affinity of Cl > F.

So Fluorine is called **Black sheep** element.

(*e*) In group 12 (Zn, Cd, Hg) value of electronegativity increases down the group, because of lanthanide contraction

(*f*) In 13th group, value of electronegativity increases down the group, because of transition contraction Electronegativity of Ga > Al.

Applications of Electronegativity

(*a*) **Metallic and non metallic nature:**

Low electronegativity $\longrightarrow$ Metals

High electronegativity $\longrightarrow$ Non metals

Metallic character increases down the group but decreases along a period.

(*b*) **Bond length:**

$$\boxed{\Delta EN \propto \frac{1}{\text{Bond length}}}$$

Here Δ EN = difference in electronegativities of bonded atoms

Ex. HF < HCl < HBr < HI (B.L.)

Note: HF has minimum bond length because of much difference in the electronegativities of H and F.

(*c*) **Bond energy, Strength and Thermal stability:**

$$\boxed{\text{Bond energy} \propto \text{Electronegativity difference}}$$

HF > HCl > HBr > HI (B.E.)

NH_3 > PH_3 > AsH_3 (stability)

$\longrightarrow$

(*d*) **Acidic strength of hydrides:** It increases with decrease in difference of electronegativity.

Down the group, thermal stability decreases, so acidic character increases.

Order of acidic strength

HF < HCl < HBr < HI

(*e*) **Nature of bonds:**

According to Hannay & Smith formula

Ionic % = $16(X_A - X_B) + 3.5(X_A - X_B)^2$

Here X_A = Electronegativity of A

X_B = Electronegativity of B

Note:

If $X_A - X_B \geq 2.1$, Ionic % > 50% i.e. Predominant ionic bond

If $X_A - X_B < 2.1$, Ionic % < 50% i.e. Predominant covalent bond

(*f*) **Nature of hydroxides:**

(*i*) As per Gallis, In AOH, if electronegativity of A is more than 1.7 (Non metal) then it is acidic in nature.

(*ii*) If electronegativity of 'A' is less than 1.7 (metal) then AOH will be basic in nature.

eg.	NaOH	ClOH
X_A	0.9	3.0
Nature	Basic	Acidic

(*g*) **Nature of oxides:** Consider an oxide AO

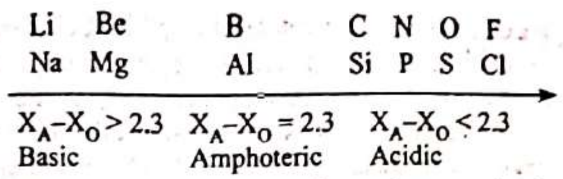
If $X_A - X_O > 2.3$, Basic oxide

If $X_A - X_O = 2.3$, Amphoteric oxide

If $X_A - X_O < 2.3$, Acidic oxide

(*i*) Along a period, acidic nature increases.

(*ii*) Down the group, basic nature increases.



ie. when in periodic table the distance between the element and oxygen increases, basic character increases.

$NO_2 > ZnO > K_2O$

$\xrightarrow{\hspace{3cm}}$

acidic character decreases

Key Note

- ❖ BeO, Al_2O_3, ZnO, SnO, PbO, SnO_2, PbO_2, Sb_2O_3 etc. are amphoteric oxides.
- ❖ CO, H_2O, NO, N_2O etc. are neutral oxides.

Acidic strength of oxide and oxyacid $\propto$ Electronegativity

- ❖ B_2O_3 CO_2 N_2O_5

$\xrightarrow{\hspace{4cm}}$

EN increase, acidic nature increase.

Order of acidic nature:

1. $SO_3 > SeO_3 > TeO_3$
2. $H_2SO_4 > H_2SeO_4 > H_2TeO_4$
3. $H_2SO_3 > H_2SeO_3 > H_2TeO_3$
4. $HNO_3 > H_2CO_3 > H_3BO_3$
5. $H_3PO_4 > H_3AsO_4 > H_3SbO_4$
6. $HOF > HOCl > HOBr > HOI$
7. $HClO_4 > HBrO_4 > HIO_4$
8. $N_2O_5 > P_2O_5 > As_2O_5$
9. $N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3$
10. $HClO_4 > HClO_3 > HClO_2 > HClO$
11. $HNO_3 > HNO_2$
12. $H_2SO_4 > H_2SO_3$
13. $N_2O_5 > N_2O_3$
14. $SO_3 > SO_2$
15. $Sb_2O_5 > Sb_2O_3$

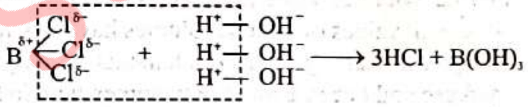
Acidic nature $\propto$ oxidation state

(*h*) Hydrolysis of AX:

Where A = Other element and X = Halogen

(*a*) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX.

eg. (BCl_3), Electronegativity of Cl > Electronegativity of B



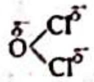
$PCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_3$

$PCl_5 + H_2O \longrightarrow 2HCl + POCl_3$

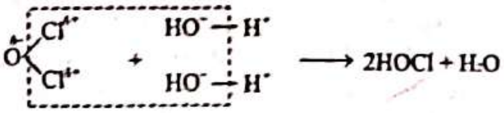
$POCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_4$

(*b*) If electronegativity of X < electronegativity of A then on hydrolysis, product will be HOX (hypohalous acid)

Ex. Cl_2O, Here electronegativity of O > Cl



So On hydrolysis –



(*i*) Nomenclature of inorganic compounds:

Prefix —— less electronegative element

Suffix —— More electronegative element

eg. Cl_2O(Right), OCl_2(Wrong)

In Dichloroxide the electronegativity of Cl is less than 'O' i.e. why Cl is in prefix position.

OF_2 - Oxygen difluoride

ICl - Iodine chloride

NH_3 - Exception (Here H is less electronegative but it is suffix)

PERIODIC TRENDS IN CHEMICAL PROPERTIES

The elements in the periodic table show chemical properties with striking periodicity. Here we shall discuss the periodicity of the valence state shown by elements and anomalous behaviour of the elements of the second period (from lithium to fluorine).

(*a*) **Chemical reactivity:** The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (**note:** noble gases having completely filled shells have rather positive electron gain enthalpy values). This results in high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. The metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period.

(*b*) **Periodicity of Valence or Oxidation States:** The valence electrons determine the valence or the valency of the atom. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals (s and p-block elements) or equal to eight minus the number of outermost electrons as shown below.

Group	1	2	13	14	15	16	17	18
Number of Valencey electron	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3,5	2,6	1,7	0,8

In contrast, transition and inner transition elements, exhibit variable valence due to involvement of not only valence electrons but d or f-electrons as well.

(*i*) **Variation along a period:** Observing the number of valence electrons from left to right, it increases from 1 to 8. But the valence of element w.r.t. H or O first increases from 1 to 4 and then decreases to zero. These trends are observed in the valency of element in hydrides and oxides are given below in the table.

Table: Periodic trends in valence of elements as shown by the formulas of their compounds

Group	1	2	13	14	15	16	17
Formula	LiH		B_2H_6	CH_4	NH_3	H_2O	HF
of hydride	NaH	CaH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
	KH			GeH_4	AsH_3	H_2Se	HBr
				SnH_4	SbH_3	H_2Te	HI
Formula	Li_2O	MgO	B_2O_3	CO_2	N_2O_5	—	
of oxide	Na_2O	CaO	Al_2O_3	SiO_2	P_4O_6, P_4O_{10}	SO_3	Cl_2O_7
	K_2O	SrO	Ga_2O_3	GeO_2	As_2O_3 As_2O_5	SeO_3	—
		BaO	In_2O_3	SnO_2	Sb_2O_3, Sb_2O_5	TeO_3	—
				PbO_2	Bi_2O_3	—	

(*ii*) **Variation within a group:** When we move down the group, the number of valence electrons remains the same, therefore all the elements in a group exhibit the same valency.

(*c*) **Anomalous Properties of Second Period Elements:** The first element of each of the groups 1 (lithium) and 2 (beryllium) and group 13-17 (boron to fluorine) differs in many respect from the other members of their respective groups. For example, lithium unlike other elements of the alkali metals and beryllium unlike other elements of the alkaline earth metals, form compounds with significantly covalent character whereas other members of their respective groups form ionic compounds.

The reasons attributed to the various anomalous chemical behaviour of the first member of a particular group of elements in the s and p-blocks compared to the other members of the same group are due to their (*i*) small size (*ii*) large charge/radius ratio (*iii*) high electronegativity of the elements (*iv*) absence of valence d-orbitals.

The first member of each group has only four valence orbitals (i.e., one 2s and three 2p-orbitals) available for bonding and hence, at the maximum 8 electrons can be accommodated. Whereas the second member of these groups have nine orbitals (i.e., one 3s, three 3p, five 3d) and hence, can accommodate more than 8 electrons. As a result the maximum covalency of first member of each group is 4, e.g., boron forms $[BF_4]^-$ whereas other members of the group can have maximum covalency of six, e.g., aluminium forms $[AlF_6]^{3-}$.

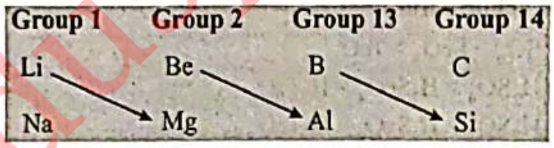
Further more, the first member of p-block elements because of smaller size and higher electronegativity, displays a greater ability to form pπ-pπ multiple bonds either with itself (e.g., $C = C$, $C \equiv C$, $N = N$, $N \equiv N$) or with other elements of the second period (e.g., $C = O$, $C = N$, $C \equiv N$, $N = O$) as compared to the subsequent members of the same group.

(*d*) **Typical Elements:** Third period elements are called as typical elements. These include Na, Mg, Al, Si, P, S, Cl.

The properties of all the elements belonging to a particular group resemble the properties of the corresponding typical element of that group. **For example**, the general properties of alkali metals (Grp. 1) can be predicted from the properties of Na, not Li, the first member of the group.

(*e*) **Diagonal relationship:** On observation it had been found that the certain elements of second period have a striking similarity with the elements of the third period placed diagonally to each other, though belonging to different groups. The behaviour of lithium and beryllium is more similar to magnesium and aluminium respectively. This similarity in properties of elements placed diagonally to each other is called **diagonal relationship** in periodic properties.

For Example



Diagonal relationship is due to similar size of ions and almost similar electronegativities of the elements or more correctly is due to similar polarizing power of ions (i.e. charge/size ratio).

(*f*) **Nature of Oxide:** The normal oxides of the elements at the extreme left of the periodic table are most basic in nature. On the other hand, the elements at the extreme right react with oxygen to form most acidic oxides. Oxides of the elements in the centre are amphoteric or neutral.

Hence, on moving across a period, the basic character of the oxides gradually changes first into amphoteric and finally into acidic character.

Also,. on moving down a group, reverse behaviour is observed i.e., from more acidic to more basic.

For example, Na_2O is strongly basic whereas Cl_2O_7 is strongly acidic. Al_2O_3 is amphoteric while CO, NO and N_2O are neutral.

(*g*) **Melting and boiling points:** The melting points of the elements exhibit some periodicity with rise of atomic number. It is observed that elements with low values of atomic volumes have high melting points while elements with high values of atomic volumes have low melting points. In general, melting points of elements in any periodic at first increase and become maximum somewhere in the center and thereafter begins to decrease.

Tungsten has the maximum melting point (3410°C) amongst metals and carbon has the maximum melting point (3727°C) amongst non-metals. Helium has the minimum melting point (–270°C). The metals, Cs, Ga and Hg are known in liquid state at 30°C.

The boiling points of the elements also show similar trends; however, the regularities are not so striking as noted in the case of melting points.

(*h*) **Nature of Hydrides:**

(*i*) Hydrogen combines with a number of other elements including metals and non-metals to form compounds called hydrides.

(*ii*) Covalent nature of hydrides increases across a period and decreases down the group.

(*iii*) Ionic hydride are better reducing agents than covalent hydrides and reducing nature of hydride decreases across a period and increases down the group.

(*i*) **Oxidising and Reducing Power :** Tendency to lose electrons and reducing power are directly related to each other; while tendency to gain electrons and oxidising power are directly related to each other.

(*i*) Down the group, the reducing character generally increases. Thus among alkali metals (except francium), cesium is the most powerful reducing element (in absence of water).

(*ii*) The reducing character decreases and oxidising character increases along the period from left to right. Thus alkali metals are strong reducing agents while halogens are oxidising agents among halogens, fluorine is the most powerful oxidising agent; the oxidising property decreases from F to I and actually iodine shows reducing properties.

(*iii*) Inert gases are neither oxidising nor reducing agents.

(*iv*) Generally, metals are reducing agents and non-metals are oxidising agents.

Train Your Brain

Example 12: Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Sol. Na_2O with water to form a strong base whereas Cl_2O_7 forms strong acid.

$Na_2O + H_2O \rightarrow 2NaOH$

$Cl_2O_7 + H_2O \rightarrow 2HClO_4$

Their basic or acidic nature can be qualitatively tested with litmus paper.

Example 13: Arrange the given oxides in increasing order of acidic nature:

B_2O_3, P_4O_{10}, SO_3, Cl_2O_7

Sol. Acidic nature of oxide $\propto$ non-metallic nature of element

$B_2O_3 < P_4O_{10} < SO_3 < Cl_2O_7$

Concept Application

17. Which is not the correct order of electronegativity?

(*a*) $Cl > S > P > Si$

(*b*) $Si > Al > Mg > Na$

(*c*) $F > Cl > Br > I$

(*d*) None of these

18. Which of the following acid is the strongest?

(*a*) HF (*b*) H_2O (*c*) NH_3 (*d*) CH_4

> *"Resilience is accepting your new reality, even if it's less good than the one you had before."*
> *– Elizabeth Edwards*

Aarambh (Solved Examples)

1. Elements A, B, C, D and E have the following electronic configurations :

A : $1s^2 2s^2 2p^1$ B : $1s^2 2s^2 2p^6 3s^2 3p^1$

C : $1s^2 2s^2 2p^6 3s^2 3p^3$ D : $1s^2 2s^2 2p^6 3s^2 3p^5$

E : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Which among these will belong to the same group in the periodic table?

Sol. Out of these, elements A and B will belong to the same group of the periodic table because they have same outer electronic configuration, $ns^2\ np^1$.

2. Select from each group the species which has the smallest radius stating appropriate reason.

(*a*) O, O^-, O^{2-} (*b*) P^{3+}, P^{4+}, P^{5+}

Sol. (*a*) O is having smallest radius. Anion is larger than its parent atom. Also the anion of the same atom with higher negative charge is bigger in size as compared to anion with smaller negative charge as proton to electron ratio decreases thus attraction between valence shell electrons and nucleus decreases. Hence electron cloud expands.

(*b*) The ionic radius decreases as more electrons are ionized off that is as the valency increases. So the correct order is $P^{5+} < P^{4+} < P^{3+}$.

3. Mg^{2+} is smaller than O^{2-} in size, though both have same electronic configuration. Explain?

Sol. Mg^{2+} and O^{2-} both are isoelectronic i.e., have same number of electrons. But Mg^{2+} having 12 protons in its nucleus exerts higher effective nuclear charge than O^{2-} having 8 protons and thus valence shell as well as inner shell electrons are more strongly attracted by the nucleus in Mg^{2+} resulting in smaller size than O^{2-}.

4. From each set, choose the atom which has the largest ionization enthalpy and explain your answer with suitable reasons.

(*a*) F, O, N (*b*) Mg, P, Ar

Sol. (*a*) Fluorine (F) has the largest ionization enthalpy because in moving from left to right in a period, atomic size decreases and electrons are held more tightly. F has the smallest size and maximum nuclear charge among given elements.

(*b*) Argon (Ar) has the largest ionization enthalpy as argon has extra stable fully filled configuration.

5. First and second ionisation energies of magnesium are 7.646 eV and 15.035 eV respectively. The amount of energy in kJ needed to convert all the atoms of magnesium into Mg^{2+} ions present in 12 mg of magnesium vapour will be? [Given 1 eV = 96.5 kJ mol^{-1}].

Sol. Total energy needed to convert one Mg atom into Mg^{2+} gas ion,

$= IE_I + IE_{II} = 22.681\ eV = 2188.6\ kJ\ mol^{-1}$.

$\Rightarrow$ 12 mg of Mg = 0.5×10^{-3} mole.

$\therefore$ Total energy = $0.5 \times 10^{-3} \times 2188.6 = 1.0943$ kJ

Therefore, [1.0943] is the correct answer.

6. $M(g) \longrightarrow M^+(g) + e^-$; $\Delta H = 100$ eV.

$M(g) \longrightarrow M^{2+}(g) + 2e^-$; $\Delta H = 250$ eV.

Which is/are correct statement(s)?

(*a*) IE_1 of M(g) is 100 eV.

(*b*) IE_1 of M^+ (g) is 150 eV.

(*c*) IE_2 of M(g) is 250 eV.

(*d*) IE_2 of M(g) is 150 eV.

Sol. $M(g) \longrightarrow M^+(g) + e^-$ IE_1 of M

$M^+ \longrightarrow M^{2+} + e^-$ IE_2 of M but IE_1 of M^+

$M \longrightarrow M^{2+} + 2e^-$ $(IE_1 + IE_2)$

Therefore, (*a*, *b*, *d*) are the correct statements.

7. Consider the elements N, P, O and S and arrange them in order of increasing negative electron gain enthalpy.

Sol. Order of increasing negative electron gain enthalpy is $N < P < O < S$.

8. Why do halogens have high electron gain enthalpies (i.e. $-\Delta_{eg}H^{\ominus}$)?

Sol. The valence shell electronic configuration of halogens is ns^2np^5 and thus they require one electron to acquire the stable noble gas configuration ns^2np^6. Because of this they have strong tendency to accept an additional electron and hence have high electron gain enthalpies.

9. Following are the valence shell electronic configurations of some elements.

(i) $3s^2\ 3p^5$ (ii) $3d^{10}\ 4s^2$

(iii) $2s^2\ 3p^6\ 4s^1$ (iv) $1s^2$

Find out the blocks to which they belong in the periodic table?

Sol. The block of the elements depend on the type of sub-shell which receive the last electron. In case of (i) it enters in 3p-subshell, (ii) it enters 3d-subshell, (iii) it enters 4s-subshell and (iv) it belongs to noble gas Helium which are kept in p-block.

Therefore, (i) p-block (ii) d-block (iii) s-block (iv) p-block, is the correct answer.

10. Arrange the following ions in the increasing order of their size : $Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-$?

Sol. Be^{2+} is smaller than Mg^{2+} as Be^{2+} has one shell where as Mg^{2+} has two shells.

Mg^{2+} and Na^+ are isoelectronic species: Ionic radius $\propto$1/nuclear charge.

Cl^- and S^{2-} are isoelectronic species : Ionic radius $\propto$ 1/nuclear charge.

Cl^- is smaller than Br^- as Cl^- has three shells where as Br^- has four shells.

Therefore, the correct order is $Be^{2+} < Mg^{2+} < Na^+ < Cl^- < S^{2-} < Br^-$

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11. The (IE_1) and the (IE_2) in kJ mol^{-1} of a few elements designated by Roman numerals are shown below:

	I	II	III
IE_1	403	549	1142
IE_2	2640	1060	2080

Which of the above elements is likely to be a

(*a*) non-metal (*b*) alkali metal

(*c*) alkaline earth metal?

Sol. (*a*) non-metal(III) – Due to highest ionisation energy, (IE_1) and (IE_2).

(*b*) alkali metal(I) – Due to lowest ionisation energy, (IE_1) and there is quite high jump in (IE_2) due to inert gas configuration of monovalent cation.

(*c*) alkaline earth metal (II) – There is little difference in (IE_1) and (IE_2) and the value of (IE_1) is slightly greater than(I) due to stable configuration(ns^2).

12. In Column-I, there are given electronic configurations of some elements. Match these with the correct metals given in Column-II:

Column-I		Column-II	
(A)	ns^2, np^5	(p)	Chromium
(B)	$(n-1)\ d^{10}, ns^1$	(q)	Copper
(C)	$(n-1)\ d^5, ns^1$	(r)	Krypton
(D)	$(n-1)\ d^{10}, ns^2, np^6$	(s)	Bromine

Sol. (A) ns^2np^5 is general valence shell electronic configuration of halogens. So this configuration belongs to Bromine.

(B) As it contains $(n-1)\ d^{10}ns^1$ configuration, it belongs to Copper.

(C) As it contains $(n-1)\ d^5ns^1$ configuration, it belongs to Chromium.

(D) Noble gases has valence shell electronic configuration $ns^2\ np^6$, so it belongs to Krypton.

Therefore, (A)→(s); (B) → (q) ; (C) → (p) ; (D) → (r) are the correct answer.

13. Match the metals given in Column-II with their type given in Column-I:

Column-I		Column-II	
(A)	Representative element	(p)	Cerium
(B)	Lanthanide	(q)	Aluminum
(C)	Coinage metal	(r)	Thorium
(D)	Actinide	(s)	Gold

Sol. (A) s-block and p-block elements are collectively called as representative elements. In aluminium last electron enters in p-subshell ($[Ne]^{10}3s^23p^1$).

(B) Lanthanide series follows lanthanum (atomic number 57) and starts from cerium (atomic number 58) to lutetium (atomic number 71), fourteen 4f- series elements.

(C) Group 11- transition elements copper, silver & Gold are known as coinage metals (used for making the coins).

(D) Actinides series follows actinium (atomic number 89) and starts from thorium (atomic number 90) to lawrencium (atomic number 103), fourteen 5f- series elements.

Therefore, (A) → (q) ; (B) → (p) ; (C) → (s) ; (D) → (r) are the correct answer.

14. Match the particulars given in Column-I with the process/ metal / species given in Column-II.

Column-I		Column-II	
(A)	Isoelectronic species	(p)	$A^+(g) + \text{energy} \rightarrow A^{++}(g) + e^-(g)$
(B)	Half filled orbital	(q)	Ar, K^+, Ca^{++}
(C)	Second ionisation energy	(r)	Lutetium
(D)	Inner transition element	(s)	Antimony

Sol. (A) Species having same number of electrons but different nuclear charge are called isoelectronic species. Ar, K^+ & Ca^{++} have same number of electrons i.e. 18 but 18, 19 & 20 number of protons respectively.

(B) np^3, $(n-1)\ d^5$ and $(n-2)\ f^7$ represent half filled orbitals. Antimony has ($[Kr]^{36}\ 4d^{10}5s^25p^3$).

Therefore, (A) → (q) ; (B) → (s) ; (C) → (p) ; (D) → (r) are the correct answer.

15. Match the type of elements / characteristic of the elements listed in Column-I with the correct element listed in Column-II.

Column-I		Column-II	
(A)	Highest 1st ionisation energy	(p)	Technetium
(B)	Highest electronegativity	(q)	Lithium
(C)	Synthetic element	(r)	Helium
(D)	Strongest reducing agent	(s)	Fluorine

Sol. (A) Helium has highest 1st ionisation energy amongst all the elements of periodic table because of ns^2 valence electron configuration and its small size of atom.

(B) Fluorine has highest electronegativity i.e. 4.0 on Pauling scale on account of its small size.

(C) Technetium is a man made element.

(D) Lithium is a strongest reducing agent because of its highest negative value of E° due to its higher hydration energy on account of its small size of atom.

Therefore, (A) → (r) ; (B) → (s) ; (C) → (p) ; (D) → (q) are the correct answer.

16. Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character:

Si, Be, Mg, Na, P.

Sol. Metallic character increases down a group and decreases in a period as we move from left to right.

Hence, the order of increasing metallic character is :

$P < Si < Be < Mg < Na$.

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. Dobereiner triads is
   (*a*) Na, K, Rb (*b*) Mg, S, As
   (*c*) Cl, Br, I (*d*) P, S, As

2. The number of elements in the 5th period of the periodic table are
   (*a*) 8 (*b*) 10
   (*c*) 18 (*d*) 32

3. Which of the following is the name of element having atomic number 103?
   (*a*) Lawrencium (*b*) Dubnium
   (*c*) Kurchatovium (*d*) Ytterbium

4. Which of the following electronic configuration is of transition elements?
   (*a*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
   (*b*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$
   (*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
   (*d*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

5. An element of atomic number 29 belongs to
   (*a*) s-block (*b*) p-block
   (*c*) d-block (*d*) f-block

6. The elements which occupy the peaks of ionisation enthalpy curve are
   (*a*) Na, K, Rb, Cs (*b*) Na, Mg, Cl, I
   (*c*) Cl, Br, I, F (*d*) He, Ne, Ar, Kr

7. The correct order of electron affinity of halogens is:
   (*a*) $F > Cl > Br > I$ (*b*) $I > Br > Cl > F$
   (*c*) $Cl > F > Br > I$ (*d*) $Cl < F > Br > I$

8. Identify the correct order of the size of the following
   (*a*) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
   (*b*) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
   (*c*) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$
   (*d*) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
(*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
(*c*) Assertion is True but the Reason is False.
(*d*) Assertion is False but Reason is True.

9. **Assertion:** Electron gain enthalpy always becomes less negative as we go down a group.
   Reason: Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

10. **Assertion:** The electron gain enthalpy of chlorine is more negative than that of fluorine.
    Reason: The fluorine atom is much larger in size than tha of chlorine.

MATCH THE COLUMN TYPE QUESTIONS

11. Match atomic number of the element given in Column-I with their position in the periodic table given in Column-II.

Column-I		Column-II	
A.	60	(p)	s-Block
B.	47	(q)	p-Block
C.	56	(r)	d-Block
D.	52	(s)	f-Block

(*a*) A-(r), B-(s), C-(q), D-(p)
(*b*) A-(s), B-(r), C-(p), D-(q)
(*c*) A-(p), B-(q), C-(s), D-(r)
(*d*) A-(q), B-(p), C-(r), D-(s)

12. Match the type of element given in Column-I with their general electronic configuration given in Column-II.

Column-I (Type of element)		Column-II (General Elect. Config.)	
A.	Noble gases	(p)	ns^1 to $ns^2\ np^5$
B.	Normal elements	(q)	ns^2, $ns^2\ np^6$
C.	Transition elements	(r)	$(n-2)f^{1-14}\ (n-1)\ d^{0-1}\ ns^2$
D.	Inner-transition elements	(s)	$(n-1)\ d^{1-10}\ ns^{1-2}$

(*a*) A-(q), B-(r), C-(p), D-(s)
(*b*) A-(p), B-(s), C-(q), D-(r)
(*c*) A-(r), B-(p), C-(s), D-(q)
(*d*) A-(q), B-(p), C-(s), D-(r)

SHORT ANSWER TYPE QUESTIONS

13. (*a*) Why is the electron gain enthalpy of fluorine not as negative as that of chlorine?
    (*b*) Which alkali metal is likely to be the least electronegative and why?

14. (*a*) Write the IUPAC name of species having atomic number:
    (i) 101
    (ii) 116
    (*b*) How would you justify the presence of 18 elements in the 5th period of the Periodic Table?

15. (*a*) What is the group and valency of the element with an atomic number of 119? Also, predict its outermost electron arrangement and the general formula of its oxide.

(*b*) Identify which pair of elements from the following list belong to the same period: Al, Si, Ba, and O.

16. (*a*) Explain why oxygen, despite having a lower ionization enthalpy than nitrogen, has a negative electron gain enthalpy while nitrogen has a positive one.

(*b*) Why noble gases have large positive electron gain enthalpy?

17. (*a*) How electronegativity is related with atomic number?

(*b*) How can you show that Na_2O is a basic oxide while Cl_2O_7 is an acidic oxide?

18. (*a*) Define the term "valence electrons" and explain how the number of valence electrons influences the chemical properties of elements within the same group in the periodic table. Provide examples to illustrate your answer?

(*b*) The first ionization enthalpy (ΔH_i) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first ΔH_i value for Al will be more close to 575 or 760 kJ mol^{-1}? Justify your answer.

LONG ANSWER TYPE QUESTIONS

19. (*a*) Explain the reason for sodium having a lower first ionization enthalpy compared to magnesium, but a higher second ionization enthalpy than magnesium.

(*b*) Provide a reason why the radius of the Na^+ cation is smaller than that of the Na atom.

20. (*a*) Explain how the metallic and non-metallic characteristics change as you move from the left to the right within a period in the periodic table.

(*b*) Arrange the elements N, P, O, and S in increasing order of their first ionization enthalpy and explain the reason behind your chosen order.

(*c*) Which one has higher electronegativity and why?

Na_2O, OF_2

21. (*a*) Arrange the following species in ascending order of their ionic radii: N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}.

(*b*) Among the given compounds, which has the highest first ionization energy:

B, Al, C, Si

(*c*) Arrange N, P, O, S in the increasing order of non-metallic character.

22. (*a*) Explain why, based on quantum numbers, the sixth period of the periodic table should consist of 32 elements.

(*b*) Determine which element, among B, Al, C, and Si, exhibits the highest metallic character, and provide a justification for your choice.

23. (*a*) What is meant by the screening or shielding effect, and how does it affect ionization enthalpy?

(*b*) Why half filled and fully filled elements have higher ionization energies as compared to other ones?

CASE STUDY BASED QUESTIONS

24. The periodic table is a fundamental tool in chemistry, organizing elements based on their atomic number and properties. Periodicity, the repeating pattern of elemental properties, plays a vital role in understanding the behavior of elements. Elements in the same group share similar chemical properties due to the same number of valence electrons, while elements in the same period exhibit gradual changes in atomic size and electronegativity. The periodic table consists of periods (rows) and groups (columns), each with its unique characteristics. The periodic table also reveals trends such as increasing electronegativity from left to right and increasing atomic size from top to bottom.

(i) Elements in the same group of the periodic table have the same number of what?

(*a*) Neutrons
(*b*) Valence electrons
(*c*) Protons
(*d*) Isotopes

(ii) In the periodic table, elements in the same period exhibit gradual changes in what two properties?

(*a*) Atomic number and mass
(*b*) Chemical reactivity and valence electrons
(*c*) Atomic size and electronegativity
(*d*) Isotopes and electron configuration

(iii) Which term refers to the repeating pattern of elemental properties in the periodic table?

(*a*) Heterogeneity
(*b*) Alkalinity
(*c*) Homogeneity
(*d*) Periodicity

(iv) Elements in the same group of the periodic table often share similar:

(*a*) Atomic masses
(*b*) Electron configurations
(*c*) Periodic numbers
(*d*) None of the above

22. IP_1 and IP_2 of Mg are 178 and 348 Kcal mol^{-1}. The enthalpy change for the reaction, $Mg \rightarrow Mg^{2+} + 2e^-$ is

(*a*) + 170 Kcal (*b*) + 526 Kcal

(*c*) – 170 Kcal (*d*) – 526 Kcal

23. The order of first ionization enthalpies of the elements Li, Be, B, Na is

(*a*) Li > Be > B > Na (*b*) Be > B > Li > Na

(*c*) Na > Li > B > Be (*d*) Be > Li > B > Na

24. Which represents alkali metals (i.e. 1st group metals) based on IE_1 and IE_2 values (in kJ/mol)?

	IE_1	IE_2
(*a*) X	500	1000
(*b*) Y	600	2000
(*c*) Z	550	7500
(*d*) M	700	1400

25. First, second and third IP values are 100eV, 150eV and corresponding 1500eV. Element can be -

(*a*) Be (*b*) B (*c*) F (*d*) Na

26. The correct values of ionization enthalpies (in kJ mol^{-1}) of Si, P, Cl and S respectively are -

(*a*) 786, 1012, 999, 1256

(*b*) 1012, 786, 999, 1256

(*c*) 786, 1012, 1256, 999

(*d*) 786, 999, 1012, 1256

27. Consider the following changes -

$A \rightarrow A^+ + e^- : E_1$ and $A^+ \rightarrow A^{2+} + e^- : E_2$

The energy required to pull out the two electrons are E_1 and E_2 respectively. The correct relationship between two energies would be

(*a*) $E_1 < E_2$ (*b*) $E_1 = E_2$

(*c*) $E_1 > E_2$ (*d*) $E_1 \geq E_2$

ELECTRON AFFINITY (ELECTRON GAIN ENTHALPY)

28. Which of the following conversion is exothermic?

(*a*) $Na \longrightarrow Na^+$ (*b*) $Li \longrightarrow Li^-$

(*c*) $N \longrightarrow N^-$ (*d*) $O \longrightarrow O^{2-}$

29. Correct order of electron affinity is:

(*a*) S > P (*b*) S < P (*c*) N > P (*d*) O > S

30. Among O, O^+, O^{2+} and O^{2-}, the species having most positive and most negative value of ΔH_{eg} are, respectively

(*a*) O^+ and O (*b*) O^{2+} and O^{2-}

(*c*) O and O^{2-} (*d*) O^{2-} and O^{2+}

31. Of the following elements, which possess the highest electron affinity?

(*a*) As (*b*) O

(*c*) S (*d*) Se

32. Correct increasing order of electron affinity for the following configuration is:

A. $1s^22s^22p^3$ B. $1s^22s^22p^4$

C. $1s^22s^22p^63s^23p^3$ D. $1s^22s^22p^63s^23p^4$

(*a*) A < C < B < D (*b*) D < A < C < B

(*c*) A < B < C < D (*d*) A < B < D < C

33. Which of the following elements has/have electron affinity greater than S?

(*a*) O (*b*) Se

(*c*) Te (*d*) None of these

34. Which of the following process is endothermic?

(*a*) $Cl \rightarrow Cl^-$ (*b*) $O \rightarrow O^-$

(*c*) $N \rightarrow N^-$ (*d*) $C \rightarrow C^-$

35. Which of the following configuration will have least electron affinity?

(*a*) ns^2np^5 (*b*) ns^2np^2

(*c*) ns^2np^3 (*d*) ns^2np^4

36. Second electron affinity of an element is

(*a*) Always exothermic

(*b*) Endothermic for few elements

(*c*) Exothermic for few elements

(*d*) Always endothermic

37. Which of the following element is expected to have highest electron affinity?

(*a*) $1s^22s^22p^63s^23p^5$ (*b*) $1s^22s^22p^3$

(*c*) $1s^22s^22p^4$ (*d*) $1s^22s^22p^5$

ELECTRONEGATIVITY AND ITS APPLICATION

38. Electronegativity of the following elements increases in the order -

(*a*) O < N < S < P (*b*) P < S < N < O

(*c*) P < N < S < O (*d*) S < P < N < O

39. Which of the following statement is incorrect?

(*a*) An element which has high electronegativity always has high electron gain enthalpy.

(*b*) Electron gain enthalpy is the property of an isolated atom.

(*c*) Electronegativity is the property of a bonded atom.

(*d*) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.

40. Which of the following statement is not true?

(*a*) F atom can hold additional electron more tightly than Cl atom.

(*b*) Cl atom can hold additional electron more tightly than F atom.

(*c*) The incoming electron encounters greater repulsion for F atom than for Cl atom.

(*d*) It is easier to remove an electron from F^- than Cl^-.

Prarambh (Topicwise)

PERIODIC TABLE

1. Three element X, Y, Z are following Doberiner's Triad rule. If the atomic weight of X and Y are 10 and 26 respectively, then atomic weight of Z will be

(*a*) 34 (*b*) 40 (*c*) 42 (*d*) 18

2. If Aufbau rule is not followed, K (Z = 19) will be placed in ______ block.

(*a*) s (*b*) p (*c*) d (*d*) f

3. In the general electronic configuration - $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$, if value of n = 7 the configuration belongs to

(*a*) Lanthanoides (*b*) Actinoides

(*c*) Transition elements (*d*) None of these

4. Given atomic number 15, 33, 51 represents the following family -

(*a*) Carbon family (*b*) Nitrogen family

(*c*) Oxygen family (*d*) None of these

ATOMIC SIZE, Z_{EFF}

5. Correct order of radius of iso-electronic species is:

(*a*) $Cl^- < S^{2-} < K^+ < Ca^{2+}$

(*b*) $S^{2-} < Cl^- < K^+ < Ca^{2+}$

(*c*) $Ca^{2+} < K^+ < Cl^- < S^{2-}$

(*d*) $K^+ < Ca^{2+} < Cl^- < S^{2-}$

6. Which of the following is generally true regarding effective nuclear charge (Z_{eff})?

(*a*) It increases on moving from left to right in a period.

(*b*) It remains almost constant on moving from top to bottom in a group.

(*c*) For isoelectronic species, as Z increases, Z_{eff} decreases.

(*d*) Both (*a*) and (*b*)

7. From the given set of species, point out the species from each set having highest Z_{eff}

(I) O^{2-}, F^-, Na^+ (II) Li, Be, Na

(III) He, Li^+, H^-

	I	II	III
(*a*)	Na^+	Be	Li^+
(*b*)	O^{2-}	Li	H^-
(*c*)	F^-	Na	He
(*d*)	Na^+	Be	He

8. The ionic radii of N^{3-}, O^{2-} and F^- are respectively given by -

(*a*) 1.36, 1.40, 1.71 (*b*) 1.36, 1.71, 1.40

(*c*) 1.71, 1.40, 1.36 (*d*) 1.71, 1.36, 1.40

9. Arrange the following element in increasing order of atomic radii:

(*a*) Na < K < Mg < Rb (*b*) K < Na < Mg < Rb

(*c*) Mg < Na < K < Rb (*d*) Rb < K < Mg < Na

10. Which of following is arranged in correct decreasing order of size?

(*a*) $Mg^{2+} > Al^{3+} > O^{2-}$ (*b*) $O^{2-} > Mg^{2+} > Al^{3+}$

(*c*) $Al^{3+} > Mg^{2+} > O^{2-}$ (*d*) $Al^{3+} > O^{2-} > Mg^{2+}$

11. In which of the following compounds, manganese show maximum radius?

(*a*) MnO_2 (*b*) $KMnO_4$

(*c*) MnO (*d*) $K_3[Mn(CN)_6]$

12. The correct order of atomic size would be

(*a*) Ni < Pd ≃ Pt (*b*) Pd < Pt < Ni

(*c*) Pt > Ni > Pd (*d*) Pd > Pt > Ni

13. Choose incorrect option regarding atomic size.

(*a*) Zr ≃ Hf (*b*) Fe ≃ Co ≃ Ni

(*c*) Y = La (*d*) All of the above

14. If the ionic radii of K^+ and F^- are nearly the same (i.e., 1.34 Å), then the atomic radii of K and F respectively are:

(*a*) 1.34 Å, 1.34 Å (*b*) 0.72 Å, 1.96 Å

(*c*) 1.96 Å, 0.72 Å (*d*) 1.96 Å, 1.34 Å

15. In which of the following pairs, atomic size of second atom is larger than the first one?

(*a*) Br, Cl (*b*) Na, Mg

(*c*) Sr, Ca (*d*) N, P

16. Which of the following configuration of atom has largest radius?

(*a*) $1s^22s^22p^63s^2$ (*b*) $1s^22s^22p^63s^23p^1$

(*c*) $1s^22s^22p^63s^23p^3$ (*d*) $1s^22s^22p^63s^23p^5$

17. The maximum tendency to form unipositive ion is for the element with the electronic configuration-

(*a*) $1s^22s^22p^63s^2$ (*b*) $1s^22s^22p^63s^23p^1$

(*c*) $1s^22s^22p^63s^23p^2$ (*d*) $1s^22s^22p^63s^23p^3$

18. If internuclear distance between Cl atoms in Cl_2 is 10 Å & between H atoms in H_2 is 2 Å, then calculate internuclear distance between H & Cl (Electronegativity of H = 2.1 & Cl = 3.0).

(*a*) 5.919 Å (*b*) 6.9 Å

(*c*) 7.919 Å (*d*) 4.91 Å

19. Which of the following is correct increasing order of paramagnetism?

(*a*) Al < Mg < O < N (*b*) Mg < Al < N < O

(*c*) Mg < Al < O < N (*d*) N < O < Al < Mg

IONISATION ENERGY (IONISATION ENTHALPY)

20. Which of the following element has highest ionisation energy?

(*a*) Oxygen (*b*) Nitrogen

(*c*) Fluorine (*d*) Helium

21. The correct order of stability of Al^+, Al^{2+}, Al^{3+} is-

(*a*) $Al^{3+} > Al^{2+} > Al^+$ (*b*) $Al^{2+} > Al^{3+} > Al^+$

(*c*) $Al^{2+} < Al^+ > Al^{3+}$ (*d*) $Al^{3+} > Al^+ > Al^{2+}$

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22. IP_1 and IP_2 of Mg are 178 and 348 Kcal mol^{-1}. The enthalpy change for the reaction, $Mg \rightarrow Mg^{2+} + 2e^-$ is

(*a*) + 170 Kcal (*b*) + 526 Kcal
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26. The correct values of ionization enthalpies (in kJ mol^{-1}) of Si, P, Cl and S respectively are -

(*a*) 786, 1012, 999, 1256
(*b*) 1012, 786, 999, 1256
(*c*) 786, 1012, 1256, 999
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$A \rightarrow A^+ + e^- : E_1$ and $A^+ \rightarrow A^{2+} + e^- : E_2$

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29. Correct order of electron affinity is:

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(*a*) O^+ and O (*b*) O^{2+} and O^{2-}
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(*c*) S (*d*) Se

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A. $1s^22s^22p^3$ B. $1s^22s^22p^4$
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(*a*) A < C < B < D (*b*) D < A < C < B
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33. Which of the following elements has/have electron affinity greater than S?

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37. Which of the following element is expected to have highest electron affinity?

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ELECTRONEGATIVITY AND ITS APPLICATION

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(*a*) O < N < S < P (*b*) P < S < N < O
(*c*) P < N < S < O (*d*) S < P < N < O

39. Which of the following statement is incorrect?

(*a*) An element which has high electronegativity always has high electron gain enthalpy.
(*b*) Electron gain enthalpy is the property of an isolated atom.
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40. Which of the following statement is not true?

(*a*) F atom can hold additional electron more tightly than Cl atom.
(*b*) Cl atom can hold additional electron more tightly than F atom.
(*c*) The incoming electron encounters greater repulsion for F atom than for Cl atom.
(*d*) It is easier to remove an electron from F^- than Cl^-.

41. Which of the following is most electronegative element?
(*a*) Li (*b*) Mg
(*c*) H (*d*) Na

42. The correct order of electronegativity on Pauling scale is:
(*a*) F > Cl > O > S (*b*) Li > Na > K > Rb > Cs
(*c*) Be < B < N < C (*d*) Both (*a*) and (*b*)

43. The order in which the following oxides are arranged according to decreasing basic nature is-
(*a*) $Na_2O > MgO > Al_2O_3 > SiO_2$
(*b*) $SiO_2 > Al_2O_3 > MgO > Na_2O$
(*c*) $Al_2O_3 > SiO_2 > MgO > Na_2O$
(*d*) $SiO_2 > MgO > Na_2O > Al_2O_3$

44. Which of the following is most acidic oxide?
(*a*) MnO (*b*) MnO_2 (*c*) Mn_2O_7 (*d*) Mn_3O_4

45. Which of the following is an amphoteric oxide?
(*a*) SnO (*b*) V_2O_5
(*c*) Cr_2O_3 (*d*) All of these

46. Which of the following elements never has an oxidation state of +1?
(*a*) F (*b*) Cl (*c*) Br (*d*) I

Prabal (JEE Main Level)

1. Which of the following is not an actinoid?
(*a*) Curium (Z = 96) (*b*) Californium (Z = 98)
(*c*) Uranium (Z = 92) (*d*) Terbium (Z = 65)

2. The period number in the long form of the periodic table is equal to:
(*a*) Magnetic quantum number of any element of the period.
(*b*) Atomic number of any element of the period.
(*c*) Maximum principal quantum number of any element of the period.
(*d*) Maximum azimuthal quantum number of any element of the period.

3. Which one of the following statements related to the modern periodic table is incorrect?
(*a*) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-subshell.
(*b*) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell.
(*c*) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.
(*d*) The block indicates value of azimuthal quantum number (ℓ) for the last subshell that received electrons in building up the electronic configuration.

4. The elements in which electrons are progressively filled in 4f-orbital are called :
(*a*) actinoids
(*b*) transition elements
(*c*) lanthanoids
(*d*) halogens

5. Which of the following statements is not correct regarding hydrogen?
(*a*) It resembles halogens in some properties.
(*b*) It resembles alkali metals in some properties.
(*c*) It can be placed in 17th group of modern periodic table.
(*d*) It cannot be placed in 1st group of modern periodic table.

6. Atomic number of Ag is 47. In the same group, the atomic numbers of elements placed above and below Ag in long form of periodic table, will be:
(*a*) 29, 65 (*b*) 39, 79
(*c*) 29, 79 (*d*) 39, 65

7. Choose the correct order of radius amongst the following:
(*a*) $O^{2-} > F^-$ (*b*) $Al^{3+} < Na^+$
(*c*) $Na^+ < N^{3-}$ (*d*) All of these

8. Which of the following option is correct for ionic radii?
(*a*) $Ti^{4+} < Mn^{7+}$ (*b*) $^{35}Cl^- < {}^{37}Cl^-$
(*c*) $K^+ > Cl^-$ (*d*) $P^{3+} > P^{5+}$

9. Arrange in the increasing order of atomic radii of the following elements: O, C, F, Cl, Br
(*a*) F < O < C < Cl < Br (*b*) F < C < O < Cl < Br
(*c*) F < Cl < Br < O < C (*d*) C < O < F < Cl < Br

10. Which group of atoms have nearly same atomic radius?
(*a*) Na, K, Rb, Cs (*b*) Li, Be, B, C
(*c*) Fe, Co, Ni (*d*) F, Cl, Br, I

11. Which of the following transitions involves maximum amount of energy?
(*a*) $M^-(g) \rightarrow M(g)$ (*b*) $M(g) \rightarrow M^+(g)$
(*c*) $M^+(g) \rightarrow M^{2+}(g)$ (*d*) $M^{2+}(g) \rightarrow M^{3+}(g)$

12. From the given information of element M:
$M(g) \rightarrow M^{3+}(g) + 3e^-, \Delta H = x$ kJ/mol
IE_1 (M) = y kJ/mol, IE_1 (M^{2+}) = z kJ/mol
The value of IE_2 (M) will be
(*a*) (x + y + z)kJ/ mol
(*b*) (x − y − z)kJ/mol
(*c*) (x − y + z)kJ/mol
(*d*) z − (x + y)kJ/mol

13. Match the elements with their corresponding IE_1.

	Column-I		Column-II (relative values)
A.	N	p.	+800 kJ/mol
B.	O	q.	+900 kJ/mol
C.	Be	r.	+1300 kJ/mol
D.	B	s.	+1400 kJ/mol

(*a*) A → q; B → r; C → p; D → s
(*b*) A → p; B → q; C → r; D → s
(*c*) A → s; B → r; C → q; D → p
(*d*) A → p; B → s; C → q; D → r

14. Choose the correct order of ionization energy for the following species.
(*a*) Sc > La > Y (*b*) Sc > Y = La
(*c*) Sc > Y > La (*d*) Sc < Y > La

15. Which of the following relation is correct with respect to first (I) and second (II) ionization enthalpies of potassium and calcium?
(*a*) $I_{Ca} > II_K$ (*b*) $I_K > I_{Ca}$
(*c*) $II_{Ca} > II_K$ (*d*) $II_K > II_{Ca}$

16. Which of the following is the correct order of ionisation enthalpy?
(I) $Be^+ > Be$ (II) $Be > Be^+$
(III) C > Be (IV) B > Be
(*a*) II, III (*b*) III, IV (*c*) I, III (*d*) I, IV

17. The correct decreasing order of the ionization potential of the following elements is -
(*a*) Ne > Cl > P > S > Al > Mg
(*b*) Ne > Cl > P > S > Mg > Al
(*c*) Ne > Cl > S > P > Mg > Al
(*d*) Ne > Cl > S > P > Al > Mg

18. Mg forms Mg(II) because
(*a*) The oxidation state of Mg is +2.
(*b*) Difference between $I.P_1$ and $I.P_2$ is greater than 16.0 eV.
(*c*) There are only two electrons in the outermost energy level of Mg.
(*d*) Difference between $I.P_1$ and $I.P_2$ is less than 11 eV.

19. The correct order of second I.E. of C, N, O and F are in the order:
(*a*) F > O > N > C (*b*) C > N > O > F
(*c*) O > N > F > C (*d*) O > F > N > C

20. Electronic configurations of four elements A, B, C and D are given below :
(i) $1s^22s^22p^6$ (ii) $1s^22s^22p^4$
(iii) $1s^22s^22p^63s^1$ (iv) $1s^22s^22p^5$
Which of the following is the correct order of increasing tendency to gain electron?
(*a*) (i) < (iii) < (ii) < (iv)
(*b*) (i) < (ii) < (iii) < (iv)

(*c*) (iv) < (ii) < (iii) < (i)

(*d*) (iv) < (i) < (ii) < (iii)

21. The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below:

$O(g) + e^- \longrightarrow O^-(g); \Delta H = -142 \text{ kJ mol}^{-1}$

$O^-(g) + e^- \longrightarrow O^{2-}(g); \Delta H = 884 \text{ kJ mol}^{-1}$

This is because:

(*a*) O^- ion has comparatively larger size than oxygen atom.

(*b*) Oxygen has high electron affinity.

(*c*) O^- ion will tend to resist the addition of another electron.

(*d*) Oxygen is more electronegative.

22. Which of the given anion is highly unstable?

(*a*) F^- (*b*) O^- (*c*) Be^- (*d*) Cl^-

23. Which of the following processes is exothermic?

(*a*) $N^- \rightarrow N$ (*b*) $N \rightarrow N^+$

(*c*) $N \rightarrow N^-$ (*d*) $N^+ \rightarrow N^{2+}$

24. The correct electron affinity order among the following is

(*a*) F > Cl (*b*) Cl > F

(*c*) S < P (*d*) N > O

25. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species ?

(*a*) Cl < F < S < O (*b*) O < S < F < Cl

(*c*) S < O < Cl < F (*d*) F < Cl < O < S

26. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be:

(*a*) –2.55 eV (*b*) –5.1 eV

(*c*) –10.2 eV (*d*) +2.55 eV

27. Which of the following statement is correct?

(*a*) Electron gain enthalpy may be positive for some elements.

(*b*) Second electron gain enthalpy always remains positive for all the elements.

(*c*) $\Delta_{eg}H(K^+) = -\text{IE}(K)$

(*d*) All of these

28. Choose the correct order of the property given below:

(*a*) $N^{3-} < O^{2-}$: Ionic radius

(*b*) N > O : First ionization energy

(*c*) N > O : Second ionization energy

(*d*) N > O : Electron affinity order

29. Which of the following is affected by the stable electronic configuration of an atom?

(A) Electronegativity

(B) Ionisation enthalpy

(C) Electron gain enthalpy

Correct answer is:

(*a*) Only electronegativity

(*b*) Only ionisation enthalpy

(*c*) Both electron gain enthalpy and ionisation enthalpy

(*d*) All of the above

30. The correct set of decreasing order of electronegativity is -

(*a*) Li, H, Na (*b*) Na, H, Li

(*c*) H, Li, Na (*d*) Li, Na, H

31. Which of the following given properties is wrong?

(*a*) Li > Na > K (Ionisation energy)

(*b*) Li < Na < K (Atomic size)

(*c*) $Li_2O < Na_2O < K_2O$ (Acidic nature)

(*d*) All of these

32. Considering the elements B, Al, Mg and K, the correct order of their metallic character is:

(*a*) B > Al > Mg > K (*b*) Al > Mg > B > K

(*c*) Mg > Al > K > B (*d*) K > Mg > Al > B

33. Which of the following is different from other three oxides?

(*a*) MgO (*b*) SnO

(*c*) ZnO (*d*) PbO

34. Which of the following compound is most acidic?

(*a*) Cl_2O_7 (*b*) P_4O_{10}

(*c*) SO_3 (*d*) B_2O_3

35. Which of the following order is wrong?

(*a*) $NH_3 < PH_3 < AsH_3 \Rightarrow$ Acidic character

(*b*) $Li < Be < B < C \Rightarrow IE_1$

(*c*) $Al_2O_3 < MgO < Na_2O < K_2O \Rightarrow$ Basic character

(*d*) $Li^+ < Na^+ < K^+ < Cs^+ \Rightarrow$ Ionic radius

. Choose the incorrect order for acidic strength.

(*a*) $CO_2 > CO$ (*b*) $SO_2 < SO_3$

(*c*) $HClO_2 > HOCl$ (*d*) $SiO_2 > CO_2$

37. Which of the following sequences is correct for decreasing order of ionic radius?

(*a*) $Se^{2-} > I^- > Br^- > O^{2-} > F^-$

(*b*) $I^- > Se^{2-} > O^{2-} > Br^- > F^-$

(*c*) $Se^{2-} > I^- > Br^- > F^- > O^{2-}$

(*d*) $I^- > Se^{2-} > Br^- > O^{2-} > F^-$

38. Successive ionization energies of an element 'X' are given below (in kCal/mol):

IP_1	IP_2	IP_3	IP_4
165	195	556	595

Electronic configuration of the element 'X' is

(*a*) $1s^22s^22p^63s^2 3p^2$ (*b*) $1s^22s^1$

(*c*) $1s^22s^22p^2$ (*d*) $1s^22s^2 2p^63s^2$

39. Which of the order for ionisation energy is correct?

(*a*) Be > B > C > N > O (*b*) B < Be < C < O < N

(*c*) B < Be < C < N < O (*d*) B < Be < N < C < O

40. Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionisation enthalpies?

(*a*) Na (*b*) Mg

(*c*) Si (*d*) P

41. The first ionisation energy of Mg, Al, P and S follows the order

(*a*) Mg < Al < P < S (*b*) Al < Mg < P < S

(*c*) Al < Mg < S < P (*d*) Mg < Al < S < P

42. Which of the following statements is wrong for the transition elements?

(*a*) Transition elements are placed from 3rd to 6th period.

(*b*) Last electron enters in (n – 1) d subshell.

(*c*) Exhibits variable valency.

(*d*) General electronic configuration is $(n-1)\ d^{1-10}\ ns^{1-2}$.

INTEGER TYPE QUESTIONS

43. If internuclear distance between A atoms in A_2 is 10Å and between B atoms in B_2 is 6Å, then calculate internuclear distance between A and B in Å. [Electronegativity difference between A and B has negligible value].

44. $A^-(g) \rightarrow A^{2+}(g)$ $\Delta H = 1100$ kJ/mol

$A(g) \rightarrow A^{2+}(g)$ $\Delta H = 1200$ kJ/mol

Electron gain enthalpy of A is P × 10^2 kJ/mol. What is the value of P?

45. The number of electrons for Zn^{2+} cation that have the value of azimuthal quantum number = 0, is ________.

46. How many of the following given oxide(s) is/are amphoteric in nature?

SnO, CaO, PbO, Al_2O_3, Na_2O, ZnO, MgO

47. In how many of the following pair(s) size of first species is greater than second species?

(Cl, Br), (Na^+, Li^+), (Se, S), (I^-, Br^-), (Ca, Mg), (S^{2-}, Cl^-)

48. How many element(s) among the following possess a positive value of electron gain enthalpy from the given element(s)?

He, Be, N, F, Cl, Li, C, Ne

49. Find the number of pairs in which $I.E_1$ of first element is greater than second element.

(N, O), (Be, B), (He, Ne), (S, P), (Mg, Na)

50. From the given element (s), how many have ionization energy less than chlorine atom?

Na, Mg, P, S, Ar, Aℓ

SINGLE CORRECT TYPE QUESTIONS

1. Consider two electronic configuration of K (Potassium) given below:

(I) K = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$ (follows n + ℓ rule)

(II) K = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1$ (violates n + ℓ rule)

Find the effective nuclear charge experienced by last electron in (I) and (II) respectively:

(*a*) 2.20, 7.40 (*b*) 2.00, 1.00

(*c*) 2.20, 1.00 (*d*) 2.20, 2.20

2. Which of the following orders is incorrect for size?

(*a*) Al ≈ Ga

(*b*) $Te^{2-} > I^- > Cs^+ > Ba^{2+}$

(*c*) $Cr^{3+} < Cr^{6+}$

(*d*) Pd ≈ Pt

3. Which of the following statements is incorrect?

(*a*) The second ionization enthalpy of oxygen element is greater than that of fluorine element.

(*b*) The third ionization enthalpy of phosphorus is greater than that of Aluminium.

(*c*) The first ionization enthalpy of Aluminium is slightly greater than that of Gallium.

(*d*) The second ionization enthalpy of copper is greater than that of zinc.

4. Choose the incorrect statement:

(*a*) In general, more the ionisation energy, more will be the electronegativity.

(*b*) Electronegativity increase means metallic character also increases.

(*c*) In general, lower will be the ionisation energy, easier will be to remove outer electron.

(*d*) Electron affinity of S is less than that of Cl.

5. Which of the following match is incorrect regarding B, Al, C and S elements?

(*a*) The highest first ionisation enthalpy : C

(*b*) The largest atomic size : Al

(*c*) The most negative electron gain enthalpy : C

(*d*) The most metallic character : Al

6. In which of the following arrangements, the sequence is not strictly according to the property written against it?

(*a*) HF < HCl < HBr < HI: increasing acid strength

(*b*) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing basic strength

(*c*) B < C < O < N: increasing first ionization enthalpy

(*d*) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

7. The chemistry of Be is very similar to that of Al even though they are placed in different groups. Its reason is that:

(*a*) Both are found together in nature.

(*b*) Both have nearly the same size.

(*c*) Both have similar electronic configurations.

(*d*) The ratio of their charge to size is nearly the same for ions.

8. In the following electronic configuration:

$$ns^2(n-1)d^{0-1}(n-2)f^{1-14}$$

If value of (n – 1) = 6 the configuration will be of:

(*a*) Lanthanides (*b*) d-block

(*c*) Actinides (*d*) s-block

9. An element with the electronic configuration $[Xe]4f^7\,5d^1\,6s^2$ lies in the:

(*a*) s-block (II-A group)

(*b*) d-block (III-B group)

(*c*) f-block (III-B group)

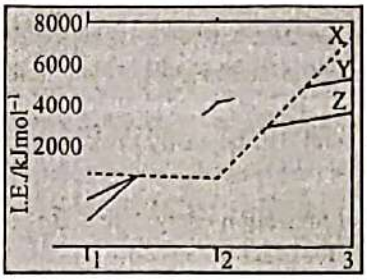
(*d*) d-block (VIII group)

10. The first and second ionization energies of Mn are in the ratio 0.475 : 1. If the sum of the two energies values is 2226 kJ/mol, calculate the second ionization energy (in kJ/mol).

(*a*) 1095 (*b*) 1960

(*c*) 1069 (*d*) 1509

11. The following qualitative plots depict the first, second and third ionization energies (I.E.) of Mg, Al and K. Among the following, the correct match of I.E. and the metal is



(*a*) X-Al; Y-Mg; Z-K (*b*) X-Mg; Y-Al; Z-K

(*c*) X-Mg; Y-K; Z-Al (*d*) X-Al; Y-K ; Z-Mg

12. Which of the following orders for electron affinity is/are correct?

(A) S > O > Se (B) Cl > F

(C) S > O (D) O > S

(E) N > P (F) C > N

(*a*) A, B, C, E (*b*) A, B, C, F

(*c*) B, C, D, E (*d*) B, C, F

13. The ground state electronic configurations of the elements, U, V, W, X and Y (these symbols do not have any chemical significance) are as follows:

U. $1s^2\,2s^2\,2p^3$

V. $1s^2\,2s^2\,2p^6\,3s^1$

W. $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$

X. $1s^2\,2s^2 2p^6\,3s^2\,3p^6\,3d^5\,4s^2$

Y. $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

Determine which sequence of elements satisfy the following statements:

(i) Element forms a carbonate which is not decomposed by heating

(ii) Element is most likely to form coloured ionic compounds

(iii) Element has largest atomic radius

(iv) Element forms only acidic oxide

(*a*) V W Y U (*b*) V X Y W

(*c*) V W Y X (*d*) V X W U

14. For the reaction, $K(g) + F(g) \rightarrow K^+(g) + F^-(g)$, $\Delta H = 138$ kcal/mol.

If ionisation potential of K and electron affinity of F have a geometrical mean of 4 eV and I.P. > E.A. then value of I.P. will be approximately: (given 23 kcal/mol = 1 ev/atom)

(*a*) 8 eV/atom (*b*) 4 eV/atom

(*c*) 2 eV/atom (*d*) 6 eV/atom

15. Which of the following set has highest sum of I.E. indicated as compared to all other sets mentioned?

(*a*) I.E.$_1$ of He, I. E$_2$ of Li, I.E.$_2$ of Ca

(*b*) I.E.$_1$ of He, I.E.$_2$ of Li, I.E.$_3$ of Mg

(*c*) I.E.$_1$ of Li, He and K

(*d*) I.E.$_2$ of Na, Ba and Sr

16. If X(OH) > Y(OH) (acidic strength) where 'Y' and 'X' both belong to same group then select the correct statement

(*a*) electron gain enthalpy of 'Y' must be greater than 'X'

(*b*) atomic size of 'X' must be greater than 'Y'

(*c*) O–H bond will be easily broken in case of hydroxide of 'X'

(*d*) O–H bond will be easily broken in case of hydroxide of 'Y'

17. Variation of ionization energy Be < B < C < N < O < F is CORRECT for order of

(*a*) I.E.$_1$ of given elements

(*b*) I.E.$_2$ of given elements

(*c*) I.E.$_3$ of given elements

(*d*) I.E. of their cations which have $2s^1$ valence electronic configuration

MULTIPLE CORRECT TYPE QUESTIONS

18. Which of the following have greater Z_{eff} than Zn?

(*a*) Cu^+ (*b*) Cu^{2+}

(*c*) Fe^{3+} (*d*) Zn^{2+}

19. Which of the following ions have radius greater than F?

(*a*) H^- (*b*) Cl^-

(*c*) Br^- (*d*) I^-

20. Choose the correct ionization energy order for the given species:

(*a*) $O > S > S^- > O^-$ (*b*) $F > F^- > Cl^- > Cl$

(*c*) $O > O^- > S^- > S$ (*d*) $F > Cl > Cl^- > F^-$

21. Those elements impart colour to the flame on heating in it, the atoms of which require low energy for the ionisation (i.e. absorb energy in the visible region of spectrum). The elements of which of the following groups in modern periodic table will impart colour to the flame?

(*a*) 2 (*b*) 13

(*c*) 1 (*d*) 17

22. Which of the following elements have electron affinity greater than O?

(*a*) F (*b*) S

(*c*) Se (*d*) Cl

23. In which of the following options order of arrangement does not agree with the variation of property indicated against it?

(*a*) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)

(*b*) B < C < N < O (increasing first ionisation enthalpy)

(*c*) I < Br < Cl < F (increasing electron gain enthalpy)

(*d*) Li < Na < K < Rb (increasing metallic radius)

24. If an electron can have four values of spin quantum numbers $\left(+\frac{3}{2}, +\frac{1}{2}, -\frac{3}{2}, -\frac{1}{2}\right)$ and rest of the quantum numbers are same, which of the following statement(s) would be correct.

(*a*) Be would have been in the first period of periodic table.

(*b*) The total number of elements in the second period would have been 12.

(*c*) There would have been 36 elements in the fourth period of periodic table.

(*d*) Number of periods would have been less than the number of periods present in the modern periodic table, for the elements discovered so far.

25. Poor shielding of nuclear charge by d or f-orbital electrons is responsible for which of the following facts?

(*a*) Atomic radius of Nb (4d-series) is comparable to that of Ta (5d-series)

(*b*) The Ist ionisation enthalpy of copper is less than that of zinc

(*c*) The value of electron gain enthalpy is more negative for sulphur than for oxygen.

(*d*) The Ist ionisation energy for gold is greater than that of silver.

26. Which is/are the correct order/s of atomic radius?

(*a*) Ni > Fe > CO (*b*) Ni ≈ Fe ≈ Co

(*c*) Sc > Ti > V (*d*) Zn > Cu > Ni

27. The correct order of ionisation energies of F^-, Cl^-, F and Cl is:

(*a*) $Cl < F < Cl^- < F^-$ (*b*) $Cl^- < F^- < Cl < F$

(*c*) $F^- < Cl^- < Cl < F$ (*d*) $Cl^- < Cl < F^- < F$

28. Select correct statements among the following:

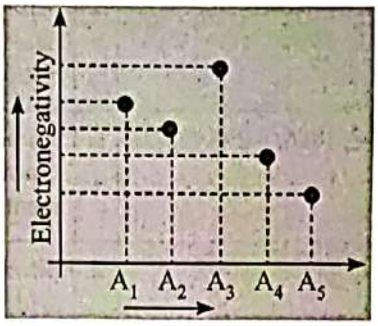
(*a*) The 1st IP of Al is less than that of Ga

(*b*) The 2nd IP of oxygen is greater than 2nd IP of F

(*c*) The 2nd IP of lithium is less than 2nd IP of oxygen

(*d*) The EA_1 of sodium is greater than EA_1 of Al

29. Following is the graph representating Electronegativity of certain elements A_1, A_2, A_3, A_4, A_5. Which of the following option(s) representing corresponding elements can be correct?



(*a*) $A_1 = N, A_2 = P, A_3 = F, A_4 = Cl, A_5 = Al$

(*b*) $A_1 = Cl, A_2 = P, A_3 = O, A_4 = N, A_5 = A_1$

(*c*) $A_1 = N, A_2 = P, A_3 = O, A_4 = Si, A_5 = Al$

(*d*) $A_1 = N, A_2 = P, A_3 = F, A_4 = Al, A_5 = Sr$

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 30 to 31): The minimum amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state is known as ionisation energy or first ionisation energy or ionisation enthalpy (IE_1) of the element. The energy required to remove the second electron from the monovalent cation is called second ionisation enthalpy (IE_2). Similarly, we have third, fourth ..... ionisation enthalpies. The values of ionisation energy depends on a number of factors such as (i) size of the atom (ii) screening effect (iii) nuclear charge (iv) half filled and fully filled orbitals.

In a group, the ionisation energy decreases from top to bottom. In a period, the value of ionisation energy generally increases from left to right except where atoms have somewhat stable configurations.

30. The electronic configurations of some neutral elements are given below

(I) $1s^2, 2s^2$ (II) $1s^2, 2s^22p^1$

(III) $1s^2, 2s^1$ (IV) $1s^2, 2s^22p^2$

Which of these electronic configurations would be expected to have highest second ionisation energy (IE_2)?

(*a*) (I) (*b*) (II)

(*c*) (III) (*d*) (IV)

31. The first (IE_1) and second (IE_2) ionisation energies (in kJ mol^{-1}) of a few elements are shown below

IE_1	IE_2
(A) 2372	5251
(B) 520	7300
(C) 900	1760
(D) 1680	3380

Which of the above elements is likely to be a noble gas?

(*a*) (A) (*b*) (B)

(*c*) (C) (*d*) (D)

Comprehension (Q 32 to 34): Atoms of metals have only a few electrons in their valence shells while atoms of non-metals generally have more electrons in their valence shells. Metallic character is closely related to atomic radius and ionisation enthalpy. Metallic character increases from top to bottom in a group and decreases from left to right in a period. Metallic character is inversely related to electronegativity.

32. Considering the elements B, C, N & F, the correct order of their non-metallic character is

(*a*) B > C > N > F (*b*) C > B > N > F

(*c*) F > N > C > B (*d*) F > B > C > N

33. The electronegativities of the following elements increase in the order

(*a*) C<N<Si<P (*b*) N<Si<C<P

(*c*) Si<P<C<N (*d*) P<Si<N<C

34. Considering the elements B, Al, Mg and K, the correct order of their metallic character is

(*a*) B>Al>Mg>K (*b*) Al>K>B>Mg

(*c*) Mg>Al>K>B (*d*) K>Mg>Al>B

Comprehension (Q 35 to 37): The first ($\Delta_i H_1$) and second ($\Delta_i H_2$) ionisation enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Element	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_{eg}H$
(A) P	520	7300	–60
(B) Q	419	3051	–48
(C) R	1681	3374	–328
(D) S	1008	1846	–295
(E) T	2372	5251	+48
(F) U	738	1451	–40

35. The least reactive element is:

(*a*) P (*b*) Q (*c*) R (*d*) T

36. The most reactive metal is:

(*a*) P (*b*) Q (*c*) S (*d*) U

37. The most reactive non-metal is:

(*a*) R (*b*) S (*c*) P (*d*) U

Comprehension (Q 38 to 40): EA_1 value of some group of p-Block elements are given below:

$$\xrightarrow{\text{At no increase}}$$

−8(a)	141(e)	328(i)
−72(b)	200(f)	349(j)
−78(c)	193(g)	325(k)
−103(d)	190(h)	295(l)

a, b, c..........ℓ are non-radioactive p-Block elements

38. Select the correct order of atomic radius:

(*a*) $a < b < c < d$ (*b*) $a < e < i$

(*c*) $i < j < k > \ell$ (*d*) $e > f > g$

39. Select the correct order of 2nd Ionisation energy:

(*a*) $a < e < i$ (*b*) $a < e < i$

(*c*) $e < a < i$ (*d*) $e > i > a$

40. Choose correct match:

(*a*) a, b, c, d = Pnictogens (*b*) e, f, g, h = Chalogens

(*c*) i, j, k, l = Halogens (*d*) All of these

MATCH THE COLUMN TYPE QUESTIONS

41. Match column-I with column-II and choose the correct answer from the code given below:

Column-I (Atomic number)		Column-II	
A.	57	p.	is a d-block or a p-block element
B.	17	q.	is 4th period element
C.	19	r.	violates Aufbau's principle
D.	29	s.	is a non-metal
		t.	is s-block element

(*a*) A – p, r; B – p, s; C – q, t; D – p, q, r

(*b*) A – s, r, q; B – t, s; C – q, s; D – p, r

(*c*) A – q, r; B – p, s; C – q, t; D – p, q

(*d*) A – p, q, r; B – t, s; C – p, s; D – t, q, r

42. Match column-I with column-II and choose the correct answer from the code given below:

Column-I		Column-II	
A.	Strongest reductant	p.	Aurum/Au^{3+}
B.	Half filled d-orbital	q.	Cerium/Ce^{3+}
C.	Coinage metal	r.	Chromium
D.	Lanthanide	s.	Iodide ion

(*a*) A – s, B – r, C – p, D – q

(*b*) A – q, B – r, C – p, D – q

(*c*) A – q, B – s, C – r, D – p

(*d*) A – p, B – q, C – r, D – s

43. Match the values of ionization energy and electron gain enthalpy listed in column-I with characteristics(s) of elements of listed in column-II.

Column-I $\Delta_i H_1, \Delta_i H_2, \Delta_{eg} H$ (in KJ mol^{-1})		Column-II	
A.	2372, 5251, +48	p.	Element which acts as a strong reducing agent
B.	419, 3051, −48	q.	Element which exists as a monoatomic molecule.
C.	1681, 3374, −333	r.	Least reactive non-metal
D.	1008, 1846, −295	s.	Element which acts as a strong oxidising agent.
		t.	Element which oxide is stronger basic in nature.

(*a*) A – q, B – p,t, C – s, D – r

(*b*) A – s,t, B – r, C – p, D – q

(*c*) A – q, B – s, C – r,t, D – p

(*d*) A – p,t, B – q, C – r, D – s

INTEGER TYPE QUESTIONS

44. What is the maximum number of electrons possible in Ni^+ having same spin?

45. Report atomic number of the element having largest size among the following:

Ni, Cu, Zn

46. The electron gain enthalpy of a hypothetical element 'A' is −3 eV per atom. How much energy (in kcal mol^{-1}) is released when 10 g of 'A' are completely converted to A^- ions in gaseous state?

(Take : 1 eV per atom = 23 kcal mol^{-1},

Molar mass of A = 30 g)

47. How many of the following radii order(s) is/are incorrect?

(i) $N^{3-} > P^{3-}$

(ii) $O^{2-} > F^-$

(iii) $Ca^{2+} > Sr^{2+}$

(iv) $S^{2-} > S$

(v) $Cl^- > S^{2-}$

48. Number of unpaired electrons in Mn^{+7} = a

Number of d-subshell electrons in Cr = b

Number of f-subshell electrons in Hf (Atomic no.: 72) = c

Find the value of c – b + a.

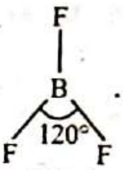
49. How many elements are possible for 1st period of periodic table if azimuthal quantum number can have integral values from 0, 1, 2, ... (n + 1)?

50. Successive IE-values IE_1, IE_2, IE_3 of element 'X' are 9.3, 18.2 and 553.8 eV per atom respectively. Predict group number of element 'X' in modern periodic table.

51. Find maximum value of $n + l + |m|$ for the last unpaired electron in an element present in 17th group and 4th period of periodic table.

52. An ion having a 4+ charge and a mass of 51.99 amu has two electrons with $n = 1$, eight electrons with $n = 2$ and ten electrons with $n = 3$. Give the total number of protons present in the nucleus of the atom of metal.

53. BF_3 molecule has the following structure



. If covalent radius of B is 0.85 Å and that of F is 0.73 Å and electronegativity of B is 2 and F is 4 then calculate the value of $\frac{100\,Y}{\sqrt{3}}$ where Y is the intermolecular distance between two nearest fluorine atoms in Å.

54. For the gaseous reaction $K + F \rightarrow K^+ + F^-$, ΔH was calculated to be 18.4 kcal/mol under conditions where the cations and anions were prevented from combining with each other. The ionisation enthalpy of K is 4.3 eV/atom. What is the electron gain enthalpy of F (in eV/atom)? If your answer is X, report it as –2X

55. Find total number of enthalpy(s) (out of given nine) of M(g) which is/are not associated with conversion of

$$M^-_{(g)} \longrightarrow M^{4+}_{(g)}$$

$I.E._1$, $I.E._2$, $I.E._3$, $I.E._4$, $I.E._5$, $I.E._6$, EGE_1, EGE_2, EGE_3
(I.E. = ionization energy, EGE = electron gain enthalpy)

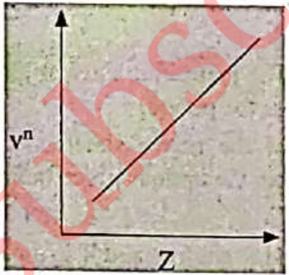
PYQ's (Past Year Questions)

MODERN PERIODIC LAW & NOMENCLATURE OF ELEMENTS

1. If IUPAC name of an element is "Unununnium" then the element belongs to nth group of periodic table. The value of *n* is______.

[30 Jan, 2024 (Shift-I)]

2. It is observed that characteristic X-ray spectra of elements show regularity. When frequency to the power 'n' i.e. v^n of X-rays emitted is plotted against atomic number 'Z', following graph is obtained. **[24 Jan, 2023 (Shift-I)]**

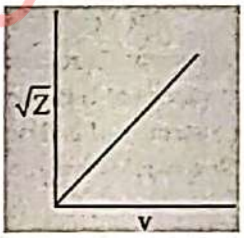


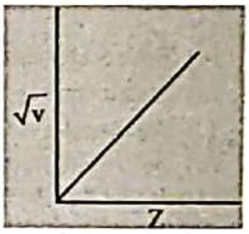
The value of 'n' is

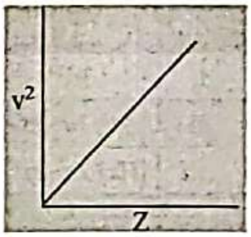
(*a*) 1 (*b*) 2

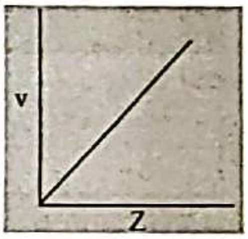
(*c*) $\frac{1}{2}$ (*d*) 3

3. Henry Moseley studied characteristic X-ray spectra of elements. The graph which represents his observation correctly is: (Given v = frequency of X-ray emitted; Z = atomic number) **[8 April, 2023 (Shift-II)]**

(*a*)


(*b*)


(*c*)


(*d*)


4. The IUPAC nomenclature of an element with electronic configuration [Rn] $5f^{14} 6d^1 7s^2$ is: **[25 July, 2022 (Shift-I)]**

(*a*) Unnilbium (*b*) Unnilunium

(*c*) Unnilquandium (*d*) Unniltrium

5. Which one of the following statements for D.I. Mendeleev's, is incorrect? **[22 July, 2021 (Shift-II)]**

(*a*) At the time, he proposed periodic table of elements structure of atom was known

(*b*) Element with atomic number 101 is named after him

(*c*) He invented accurate barometer

(*d*) He authored the textbook – Principles of Chemistry

6. The atomic number of the element unnilennium is **[03 Sept, 2020 Shift-I)]**
(*a*) 102 (*b*) 108 (*c*) 119 (*d*) 109

7. The IUPAC symbol for the element with atomic number 119 would be: **[8 April, 2019 (Shift-II)]**
(*a*) unh (*b*) uun (*c*) une (*d*) uue

ELECTRONIC CONFIGURATIONS AND TYPES OF ELEMENTS: S-, P-, D-, F- BLOCKS

8. Given below are two statements:
Statement-I: The 4f and 5f-series of elements are placed separately in the Periodic table to preserve the principle of classification.
Statement-II: s-block elements can be found in pure form in nature.
In the light of the above statements, choose the most appropriate answer from the options given below: **[27 Jan, 2024 (Shift-I)]**
(*a*) Statement-I is false but Statement-II is true
(*b*) Both Statement-I and Statement-II are true
(*c*) Statement-I is true but Statement-II is false
(*d*) Both Statement-I and Statement-II are false

9. Given below are two statements:
Statement-I: Both metal and non-metal exist in p and d-block elements.
Statement-II: Non-metals have higher ionisation enthalpy and higher electronegativity than the metals.
In the light of the above statements, choose the most appropriate answer from the option given below: **[01 Feb, 2024 (Shift-II)]**
(*a*) Both Statement-I and Statement-II are false
(*b*) Statement-I is false but Statement-II is true
(*c*) Statement-I is true but Statement-II is false
(*d*) Both Statement-I and Statement-II are true

10. Match List-I with List-II

	List-I (Element)		List-II (Electronic Configuration)
A.	N	I.	[Ar] $3d^{10}4s^2\,4p^5$
B.	S	II.	[Ne] $3s^2\,3p^4$
C.	Br	III.	[He] $2s^2\,2p^3$
D.	Kr	IV.	[Ar] $3d^{10}\,4s^2\,4p^6$

Choose the correct answer from the options given below: **[09 April, 2024 (Shift-II)]**
(*a*) A-IV, B-III, C-II, D-I (*b*) A-III, B-II, C-I, D-IV
(*c*) A-I, B-IV, C-III, D-II (*d*) A-II, B-I, C-IV, D-III

11. Match List - I with List - II. **[30 Jan, 2023 (Shift-I)]**

	List-I (Atomic number)		List-II (Block of periodic table)
A.	37	I.	p-block
B.	78	II.	d-block
C.	52	III.	f-block
D.	65	IV.	s-block

Choose the correct answer from the options given below:
(*a*) (A)-(II), (B)-(IV), (C)-(I), (D)-(III)
(*b*) (A)-(I), (B)-(III), (C)-(IV), (D)-(II)
(*c*) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)
(*d*) (A)-(IV), (B)-(II), (C)-(I), (D)-(III)

12. The total number of isoelectronic species from the given set is
O^{2-}, F^-, Al, Mg^{2+}, Na^+, O^+, Mg, Al^{3+}, F
[15 April, 2023 (Shift-I)]

13. Which one of the following sets of ions represents a collection of isoelectronic species?
(Given: Atomic Number: F : 9, Cl : 17, Na = 11, Mg = 12, Al = 13, K = 19, Ca = 20, Sc = 21) **[1 Feb, 2023 (Shift-II)]**
(*a*) Li^+, Na^+, Mg^{2+}, Ca^{2+} (*b*) Ba^{2+}, Sr^{2+}, K^+, Ca^{2+}
(c) N^{3-}, O^{2-}, F^-, S^{2-} (*d*) K^+, Cl^-, Ca^{2+}, Sc^{3+}

14. The pair, in which both ions are isoelectronic with Al^{3+} is: **[25 June, 2022 (Shift-I)]**
(*a*) Br^- and Be^{2+} (*b*) Cl^- and Li^+
(*c*) S^{2-} and K^+ (*d*) O^{2-} and Mg^{2+}

15. The element with Z = 120 (not yet discovered) will be an/a **[12 Jan, 2019 (Shift-I)]**
(*a*) Inner transition metal
(*b*) Alkaline earth metal
(*c*) Alkali metal
(*d*) Transition metal

16. The group number, number of valence electrons, and valency of an element with atomic number 15, respectively, are **[12 April, 2019 (Shift-I)]**
(*a*) 16, 5 and 2 (*b*) 16, 6 and 3
(*c*) 15, 5 and 3 (*d*) 15, 6 and 2

PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

17. Given below are two statements: One is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**:
Assertion (A): The first ionisation enthalpy decreases across a period.
Reason (R): The increasing nuclear charge outweighs the shielding across the period.
In the light of the above statements, choose the most appropriate from the options given below: **[29 Jan, 2024 (Shift-I)]**
(*a*) Both A and R are true and R is the correct explanation of A
(*b*) A is true but R is false
(*c*) A is false but R is true
(*d*) Both A and R are true but R is NOT the correct explanation of A

18. The element having the highest first ionization enthalpy is **[29 Jan, 2024 (Shift-II)]**
(*a*) Si (*b*) Al (*c*) N (*d*) C

19. Given below are two statements:

Statement-I: Fluorine has most negative electron gain enthalpy in its group.

Statement-II: Oxygen has least negative electron gain enthalpy in its group.

In the light of the above statements, choose the most appropriate from the options given below.

[29 Jan, 2024 (Shift-II)]

(*a*) Both Statement-I and Statement-II are true

(*b*) Statement-I is true but Statement-II is false

(*c*) Both Statement-I and Statement-II are false

(*d*) Statement-I is false but Statement-II is true

20. Given below are the two statements: One is labeled as **Assertion (A)** and the other is labeled as **Reason (R)**.

Assertion (A): There is a considerable increase in covalent radius from N to P. However from As to Bi only a small increase in covalent radius is observed.

Reason (R): covalent and ionic radii in a particular oxidation state increases down the group.

In the light of the above statement, choose the most appropriate answer from the options given below:

[30 Jan, 2024 (Shift-I)]

(*a*) (A) is false but (R) is true

(*b*) Both (A) and (R) are true but (R) is not the correct explanation of (A)

(*c*) (A) is true but (R) is false

(*d*) Both (A) and (R) are true and (R) is the correct explanation of (A)

21. Given below are two statements:

Statement-I: Along the period, the chemical reactivity of the element gradually increases from group 1 to group 18.

Statement-II: The nature of oxides formed by group 1 element is basic while that of group 17 elements is acidic.

In the light above statements, choose the most appropriate from the questions given below. **[30 Jan, 2024 (Shift-II)]**

(*a*) Both statement-I and Statement-II are true.

(*b*) Statement-I is true but Statement-II is False.

(*c*) Statement-I is false but Statement-II is true.

(*d*) Both Statement-I and Statement-II is false.

22. The correct sequence of electron gain enthalpy of the elements listed below is **[31 Jan, 2024 (Shift-I)]**

A. Ar B. Br C. F D. S

Choose the ***most appropriate*** from the options given below:

(*a*) $C > B > D > A$ (*b*) $A > D > B > C$

(*c*) $A > D > C > B$ (*d*) $D > C > B > A$

23. Consider the following elements.

Group ↓ **A'B'** ⟶ **Period**

C'D'

Which of the following is/are true about A', B', C' and D' ?

A. Order of atomic radii: $B' < A' < D' < C'$

B. Order of metallic character: $B' < A' < D' < C'$

C. Size of the element: $D' < C' < B' < A'$

D. Order of ionic radii: $B'^{+} < A'^{+} < D'^{+} < C'^{+}$

Choose the correct answer from the options given below:

[31 Jan, 2024 (Shift-II)]

(*a*) A only (*b*) A, B and D only

(*c*) A and B only (*d*) B, C and D only

24. In case of isoelectronic species the size of F^-, Ne and Na^+ is affected by: **[01 Feb, 2024 (Shift-I)]**

(*a*) Principal quantum number (n)

(*b*) None of the factors because their size is the same

(*c*) Electron-electron interaction in the outer orbitals

(*d*) Nuclear charge (z)

25. Lowest Oxidation number of an atom in a compound A_2B is –2. The number of electrons in its valence shell is

[01 Feb, 2024 (Shift-I)]

26. The correct order of first ionization enthalpy values of the following elements is: **[04 April, 2024 (Shift-I)]**

(A) O (B) N (C) Be (D) F

(E) B

Choose the correct answer from the options given below:

(*a*) $B < D < C < E < A$ (*b*) $E < C < A < B < D$

(*c*) $C < E < A < B < D$ (*d*) $A < B < D < C < E$

27. The correct order of the first ionization enthalpy is

[04 April, 2024 (Shift-II)]

(*a*) $Al > Ga > Tl$ (*b*) $Ga > Al > B$

(*c*) $B > Al > Ga$ (*d*) $Tl > Ga > Al$

28. Given below are two statements:

Statement-I: The correct order of first ionization enthalpy values of Li, Na, F and Cl is $Na < Li < Cl < F$.

Statement-II: The correct order of negative electron gain enthalpy values of Li, Na, F and Cl is

$Na < Li < F < Cl$

In the light of the above statements, choose the correct answer from the options given below:

[04 April, 2024 (Shift-II)]

(*a*) Both Statement-I and Statement-II are true

(*b*) Both Statement-I and Statement-II are false

(*c*) Statement-I is false but Statement-II is true

(*d*) Statement-I is true but Statement-II is false

29. The statement(s) that are correct about the species O^{2-}, F^-, Na^+ and Mg^{2+}.

(A) All are isoelectronic

(B) All have the same nuclear charge

(C) O^{2-} has the largest ionic radii

(D) Mg^{2+} has the smallest ionic radii

Choose the most appropriate answer from the options given below: **[05 April, 2024 (Shift-I)]**

(*a*) (B), (C) and (D) only (*b*) (A), (B), (C) and (D)

(*c*) (C) and (D) only (*d*) (A), (C) and (D) only

30. Given below are two statements:

Statement-I: The metallic radius of Na is 1.86 Å and the ionic radius of Na^+ is lesser than 1.86 Å.

Statement-II: Ions are always smaller in size than the corresponding elements.

In the light of the above statements, choose the correct answer from the options given below: **[05 April, 2024 (Shift-II)]**

(*a*) Statement-I is true but Statement-II is false

(*b*) Both Statement-I and Statement-II are true

(*c*) Both Statement-I and Statement-II are false

(*d*) Statement-I is false but Statement-II is true

31. The electron affinity value are negative for:

A. $Be \rightarrow Be^-$ B. $N \rightarrow N^-$

C. $O \rightarrow O^{2-}$ D. $Na \rightarrow Na^-$

E. $Al \rightarrow Al^-$

Choose the most appropriate answer from the options given below: **[06 April, 2024 (Shift-I)]**

(*a*) D and E only (*b*) A, B, D and E only

(*c*) A and D only (*d*) A, B and C only

32. Match **List-I** with **List-II**

List-I (Elements)		List-II (Properties in their respective groups)	
A.	Cl, S	I.	Elements with highest electronegativity
B.	Ge, As	II.	Elements with largest atomic size
C.	Fr, Ra	III.	Elements which show properties of both metals and non metal
D.	F, O	IV.	Elements with highest negative electron gain enthalpy

Choose the **correct** answer from the options given below: **[08 April, 2024 (Shift-I)]**

(*a*) A-II, B-III, C-IV, D-I

(*b*) A-III, B-II, C-I, D-IV

(*c*) A-IV, B-III, C-II, D-I

(*d*) A-II, B-I, C-IV, D-III

33. Identify the correct statements about p-block elements and their compounds. **[08 April, 2024 (Shift-II)]**

(A) Non metals have higher electronegativity than metals.

(B) Non metals have lower ionisation enthalpy than metals.

(C) Compounds formed between highly reactive nonmetals and highly reactive metals are generally ionic.

(D) The non-metal oxides are generally basic in nature.

(E) The metal oxides are generally acidic or neutral in nature.

(*a*) (D) and (E) only (*b*) (A) and (C) only

(*c*) (B) and (E) only (*d*) (B) and (D) only

34. Given below are two statements:

Statement-I: The oxidation state of an element in a particular compound is the charge acquired by its atom on the basis of electron gain enthalpy consideration from other atoms in the molecule.

Statement-II: pπ-pπ bond formation is more prevalent in second period elements over other periods.

In the light of the above statements, choose the most appropriate answer from the options given below: **[09 April, 2024 (Shift-I)]**

(*a*) Both Statement-I and Statement-II are incorrect

(*b*) Statement-I is correct but Statement-II is incorrect

(*c*) Both Statement-I and Statement-II are correct

(*d*) Statement-I is incorrect but Statement-II is correct

35. Given below are two statements:

Statement-I: The decrease in first ionization enthalpy from B to Al is much larger than that from Al to Ga.

Statement-II: The d orbitals in Ga are completely filled. **[29 Jan, 2023 (Shift-II)]**

In the light of the above statements, choose the most appropriate answer from the options given below

(*a*) Statement-I is incorrect but Statement-II is correct

(*b*) Both the Statements-I and II are correct

(*c*) Statement-I is correct but Statement-II is incorrect

(*d*) Both the Statements-I and II are incorrect

36. Which of the following represents the correct order of metallic character of the given elements? **[25 Jan, 2023 (Shift-II)]**

(*a*) $Si < Be < Mg < K$ (*b*) $Be < Si < Mg < K$

(*c*) $K < Mg < Be < Si$ (*d*) $Be < Si < K < Mg$

37. The difference between electron gain enthalpies will be maximum between: **[6 April, 2023 (Shift-I)]**

(*a*) Ne and F (*b*) Ne and Cl

(*c*) Ar and Cl (*d*) Ar and F

38. For elements B, C, N, Li, Be, O and F the correct order of first ionization enthalpy is **[11 April, 2023 (Shift-I)]**

(*a*) $Li < Be < B < C < N < O < F$

(*b*) $B > Li > Be > C > N > O > F$

(*c*) $Li < B < Be < C < O < N < F$

(*d*) $Li < Be < B < C < O < N < F$

39. Inert gases have positive electron gain enthalpy. Its correct order is **[25 Jan, 2023 (Shift-I)]**

(*a*) $Xe < Kr < Ne < He$ (*b*) $He < Ne < Kr < Xe$

(*c*) $He < Xe < Kr < Ne$ (*d*) $He < Kr < Xe < Ne$

40. The correct order of electronegativity for given elements is: **[8 April, 2023 (Shift-I)]**

(*a*) $C > P > At > Br$ (*b*) $Br > P > At > C$

(*c*) $P > Br > C > At$ (*d*) $Br > C > At > P$

41. The correct decreasing order for metallic character is **[28 July, 2022 (Shift-II)]**

(*a*) $Na > Mg > Be > Si > P$ (*b*) $P > Si > Be > Mg > Na$

(*c*) $Si > P > Be > Na > Mg$ (*d*) $Be > Na > Mg > Si > P$

42. Match List-I with List-II. **[26 Feb, 2021 (Shift-I)]**

	List-I Electronic configuration of elements		List-II $\Delta_i H$ (kJ mol^{-1})
A.	$1s^2 2s^2$	I.	801
B.	$1s^2 2s^2 2p^4$	II.	899
C.	$1s^2 2s^2 2p^3$	III.	1314
D.	$1s^2 2s^2 2p^1$	IV.	1402

Choose the most appropriate answer from the options given below:

(*a*) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

(*b*) (A)-(I), (B)-(III), (C)-(IV), (D)-(II)

(*c*) (A)-(I), (B)-(IV), (C)-(III), (D)-(II)

(*d*) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

43. Given below are two statements: one is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**.

Assertion (A): Metallic character decreases and non-metallic character increases on moving from left to right in a period.

Reason (R): It is due to increase in ionisation enthalpy and decrease in electron gain enthalpy, when one moves from left to right in a period. **[31 Aug, 2021 (Shift-I)]**

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) (A) is false but (R) is true

(*b*) Both (A) and (R) are correct and (R) is the correct explanation of (A)

(*c*) Both (A) and (R) are correct but (R) is not the correct explanation of (A)

(*d*) (A) is true but (R) is false

44. The ionic radii of F^- and O^{2-} respectively are 1.33 Å and 1.4 Å, while the covalent radius of N is 0.74 Å.

The correct statement for the ionic radius of N^{3-} from the following is: **[25 July, 2021 (Shift-II)]**

(*a*) It is smaller than O^{2-} and F^-, but bigger than of N

(*b*) It is bigger than F^- and N, but smaller than of O^{2-}

(*c*) It is smaller than F^- and N

(*d*) It is bigger than O^{2-} and F^-

45. The absolute value of the electron gain enthalpy of halogens satisfies: **[17 March, 2021 (Shift-I)]**

(*a*) $F > Cl > Br > I$ (*b*) $Cl > F > Br > I$

(*c*) $I > Br > Cl > F$ (*d*) $Cl > Br > F > I$

46. The ionic radius of Na^+ ion is 1.02 Å. The ionic radii (in Å) of Mg^{2+} and Al^{3+}, respectively are: **[8 March, 2021 (Shift-I)]**

(*a*) 0.85 and 0.99 (*b*) 0.68 and 0.72

(*c*) 0.72 and 0.54 (*d*) 1.05 and 0.99

47. The five successive ionization enthalpies of an element are 800, 2427, 3658, 25024 and 32824 kJ mol^{-1}. The number of valence electrons in the element is:

[3 Sept, 2020 (Shift-II)]

(*a*) 4 (*b*) 2 (*c*) 5 (*d*) 3

48. Three elements X, Y and Z are in the 3rd period of the periodic table. The oxides of X, Y and Z, respectively, are basic, amphoteric and acidic. The correct order of the atomic numbers of X, Y and Z is: **[2 Sept, 2020 (Shift-II)]**

(*a*) $X < Z < Y$ (*b*) $Z < Y < X$

(*c*) $X < Y < Z$ (*d*) $Y < X < Z$

49. B has a smaller first ionization enthalpy than Be. Consider the following statements: **[9 Jan, 2020 (Shift-I)]**

(I) it is easier to remove 2p electron than 2s electron.

(II) 2p electron of B is more shielded from the nucleus by the inner core of electrons than the 2s electrons of Be.

(III) 2s electron has more penetration power than 2p electron

(IV) atomic radius of B is more than Be (atomic number B = 5, Be = 4)

The correct statements are:

(*a*) (I), (III) and (IV) (*b*) (I), (II) and (III)

(*c*) (I), (II) and (IV) (*d*) (II), (III) and (IV)

50. In general, the properties that decreases and increase down a group in the periodic table respectively are

[9 Jan, 2019 (Shift-I)]

(*a*) Atomic radius and electronegativity

(*b*) Electron gain enthalpy and electronegativity

(*c*) Electronegativity and atomic radius

(*d*) Electronegativity and electron gain enthalpy

51. The correct option with respect to the Pauling electronegativity values of the elements is: **[11 Jan, 2019 (Shift-II)]**

(*a*) Te > Se (*b*) Ga < Ge

(*c*) Si < Al (*d*) P > S

52. The 1st, 2nd and the 3rd ionization enthalpies I_1, I_2 and I_3, of four atoms with atomic numbers n, n + 1, n + 2 and n + 3, where n < 10, are tabulated below. What is the value of n?

[JEE Adv 2020]

Atomic number	Ionization Enthalpy (kJ/mol)		
	I_1	I_2	I_3
n	1681	3374	6050
n + 1	2081	3952	6122
n + 2	496	4562	6910
n + 3	738	1451	7733

PW Challengers

PASSAGE-I

A mixture of two metals found in Mendeleev's periodic table in different groups, reacted with 56 cm^3 of di-hydrogen on heating (measured at STP conditions) to produce two ionic compounds. These compounds were allowed to react with 270 mg of water but only one third of water reacted. A basic solution was formed in which the content of hydroxides was 30% by mass and at the same time deposited a precipitate with a mass that represented 59.05% of a total mass of the products formed by the reaction. After filtration the precipitate was heated and its mass decreased by 27 mg.

When a stoichiometric amount of ammonium carbonate was added to the basic solution, a slightly soluble precipitate was obtained, at the same time ammonia was liberated and the content of hydroxides in the solution decreased to 16.81%.

1. Determine the mass and identity of the metal having greater mass in the starting mixture.
2. Determine the mass and identity of the metal having smaller mass in the starting mixture.

PASSAGE-II

Pauling gave method to calculate univalent ion radii by assuming that

(I) In ionic crystals (let M^+X^-) cations and anions are in contact of each other and sum of their radii is equal to inter ionic distance i.e.,

$$d_{(M^+-X^-)} = r_{(M^+)} + r_{(X^-)}$$

(II) The radius of an ion having noble gas configuration is inversely proportional to the effective nuclear charge felt at the periphery of the ion i.e.,

$$r_{(M^+)} = \frac{C}{Z_{\text{eff}(M^+)}} \text{ and } r_{(X^-)} = \frac{C}{Z_{\text{eff}(X^-)}}$$

Here C is constant of proportionality whose value depends on electronic configuration of ion.

$$\text{Thus, } d_{(M^+-X^-)} = \frac{C}{Z_{\text{eff}(M^+)}} + \frac{C}{Z_{\text{eff}(X^-)}}$$

Z_{eff} is the effective nuclear charge whose value can be calculated by the formula : $Z_{\text{eff}} = Z - \sigma$

Here σ is shielding constant and for neon configuration, the value of σ was found to be 4.5.

(given ; interionic distance in NaF = 231 pm)

3. The value of constant C for NaF crystal is :
(*a*) 231
(*b*) 115.5
(*c*) 614.25
(*d*) 307 25

4. The value of univalent radii for F^- as calculated by Pauling method is
(*a*) 94.5 pm
(*b*) 136.5 pm
(*c*) 111.68 pm
(*d*) 115.5 pm

5. The interionic distance by using univalent radii of Mg^{2+} and O^{2-}, as calculated by Pauling's method will be :
(*a*) 257.4 pm
(*b*) 205 pm
(*c*) 210.7 pm
(*d*) 219.6 pm

6. The actual interionic distance in MgO may be (assuming bivalent ion) :
(*a*) 205 pm
(*b*) 257.4 pm
(*c*) 276.0 pm
(*d*) can't be predicted

7. The value of 'C' for Na^+, Mg^{2+} and Al^{3+} will be in the order:
(*a*) $Al^{3+} > Mg^{2+} > Na^+$
(*b*) $Al^{3+} < Mg^{2+} < Na^+$
(*c*) $Al^{3+} = Mg^{2+} = Na^+$
(*d*) can not be compared

INTEGER TYPE QUESTIONS

8. Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years. Pure iron is easily oxidized, which limits its utilization. Element X is one of the alloying elements that is added to improve the oxidation resistance property of iron. Below is some information about the element X:
   I. In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
   II. In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
   III. The atomic mass of X is lower than that of Fe.
   What is the atomic number of element X?
9. Calculate value of Z_{eff} for valence electron in Hf^{+3}.
10. If there were more periods in the modern long form of the periodic table, then find the maximum number of elements in the 10th period.
11. If there were 9 periods in the periodic table & each orbital can have maximum 5 electrons, then find the maximum number of elements will be present in period 9?

ANSWER KEY

CONCEPT APPLICATION

1. (*d*) **2.** (*b*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*c*) **7.** (*a*) **8.** (*d*) **9.** (*d*) **10.** (*a*)
11. (*c*) **12.** (*c*) **13.** (*b*) **14.** (*b*) **15.** (*c*) **16.** (*b*) **17.** (*d*) **18.** (*a*)

SCHOOL LEVEL PROBLEMS

1. (*a*) **2.** (*c*) **3.** (*a*) **4.** (*d*) **5.** (*c*) **6.** (*c*) **7.** (*c*) **8.** (*b*) **9.** (*b*) **10.** (*c*)
11. (*b*) **12.** (*d*) **24.** (i)-(*b*), (ii)-(*c*), (iii)-(*d*), (iv)-(*b*)

PRARAMBH (TOPICWISE)

1. (*c*) **2.** (*c*) **3.** (*b*) **4.** (*b*) **5.** (*c*) **6.** (*d*) **7.** (*a*) **8.** (*c*) **9.** (*c*) **10.** (*b*)
11. (*c*) **12.** (*a*) **13.** (*c*) **14.** (*c*) **15.** (*d*) **16.** (*a*) **17.** (*b*) **18.** (*a*) **19.** (*c*) **20.** (*d*)
21. (*d*) **22.** (*b*) **23.** (*b*) **24.** (*c*) **25.** (*a*) **26.** (*c*) **27.** (*a*) **28.** (*b*) **29.** (*a*) **30.** (*d*)
31. (*c*) **32.** (*a*) **33.** (*d*) **34.** (*c*) **35.** (*c*) **36.** (*d*) **37.** (*a*) **38.** (*b*) **39.** (*a*) **40.** (*a*)
41. (*c*) **42.** (*b*) **43.** (*a*) **44.** (*c*) **45.** (*d*) **46.** (*a*)

PRABAL (JEE MAIN LEVEL)

1. (*d*) **2.** (*c*) **3.** (*b*) **4.** (*c*) **5.** (*d*) **6.** (*c*) **7.** (*d*) **8.** (*d*) **9.** (*a*) **10.** (*c*)
11. (*d*) **12.** (*b*) **13.** (*c*) **14.** (*c*) **15.** (*d*) **16.** (*c*) **17.** (*b*) **18.** (*d*) **19.** (*d*) **20.** (*a*)
21. (*c*) **22.** (*c*) **23.** (*a*) **24.** (*b*) **25.** (*b*) **26.** (*b*) **27.** (*d*) **28.** (*b*) **29.** (*c*) **30.** (*c*)
31. (*c*) **32.** (*d*) **33.** (*a*) **34.** (*a*) **35.** (*b*) **36.** (*d*) **37.** (*d*) **38.** (*d*) **39.** (*b*) **40.** (*a*)
41. (*c*) **42.** (*a*) **43.** [8] **44.** [1] **45.** [6] **46.** [4] **47.** [5] **48.** [4] **49.** [4] **50.** [5]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*c*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*c*) **6.** (*b*) **7.** (*d*) **8.** (*c*) **9.** (*c*) **10.** (*d*)
11. (*c*) **12.** (*d*) **13.** (*b*) **14.** (*a*) **15.** (*b*) **16.** (*c*) **17.** (*d*) **18.** (*a,b,c,d*) **19.** (*a,b,c,d*) **20.** (*a,d*)
21. (*a,c*) **22.** (*a,b,c,d*) **23.** (*b,c*) **24.** (*a,c,d*) **25.** (*a,d*) **26.** (*b,c*) **27.** (*c*) **28.** (*a,b,d*) **29.** (*c,d*) **30.** (*c*)
31. (*a*) **32.** (*c*) **33.** (*c*) **34.** (*d*) **35.** (*d*) **36.** (*b*) **37.** (*a*) **38.** (*a*) **39.** (*d*) **40.** (*d*)
41. (*a*) **42.** (*b*) **43.** (*a*) **44.** [15] **45.** [30] **46.** [23] **47.** [3] **48.** [9] **49.** [8] **50.** [2]
51. [6] **52.** [24] **53.** [1.40] **54.** [7] **55.** [4]

PYQ's (PAST YEAR QUESTIONS)

1. [11] **2.** (*c*) **3.** (*b*) **4.** (*d*) **5.** (*a*) **6.** (*d*) **7.** (*d*) **8.** (*c*) **9.** (*b*) **10.** (*b*)
11. (d) **12.** [5] **13.** (*d*) **14.** (*d*) **15.** (*b*) **16.** (*c*) **17.** (*c*) **18.** (*c*) **19.** (*d*) **20.** (*b*)
21. (*c*) **22.** (*b*) **23.** (*b*) **24.** (*d*) **25.** [6] **26.** (*b*) **27.** (*d*) **28.** (*a*) **29.** (*d*) **30.** (*a*)
31. (*d*) **32.** (*c*) **33.** (*b*) **34.** (*d*) **35.** (*b*) **36.** (*a*) **37.** (*b*) **38.** (*c*) **39.** (*c*) **40.** (*d*)
41. (*a*) **42.** (*a*) **43.** (*d*) **44.** (*d*) **45.** (*b*) **46.** (*c*) **47.** (*d*) **48.** (*c*) **49.** (*b*) **50.** (*c*)
51. (*b*) **52.** [9]

PW CHALLENGERS

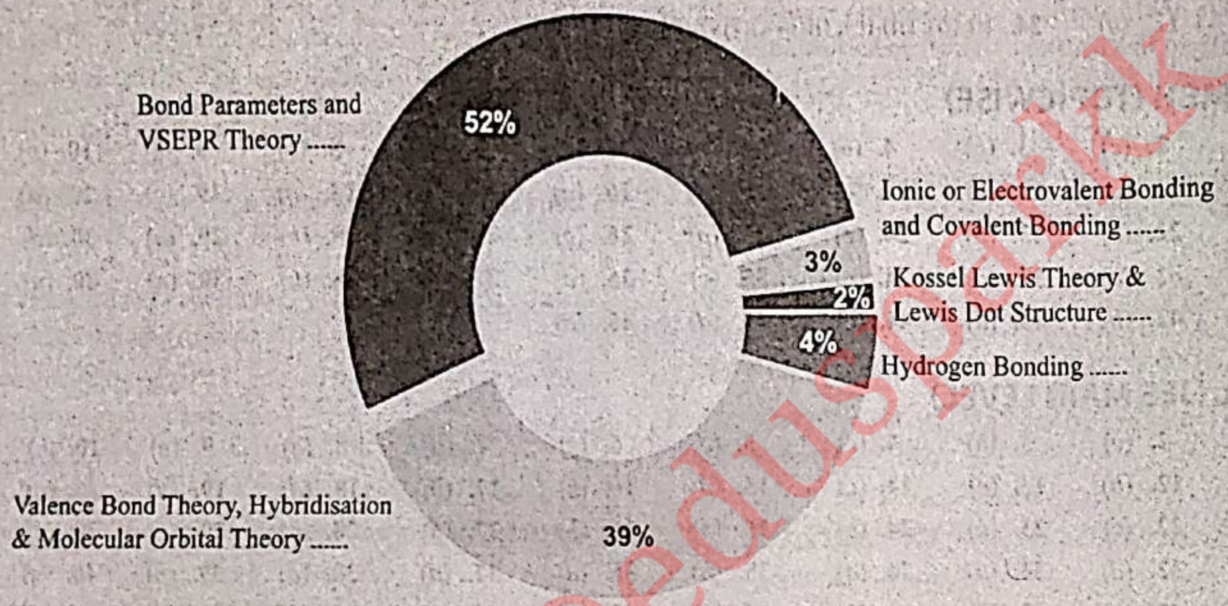
1. [0.080 g Ca] **2.** [0.023 g Na] **3.** (*c*) **4.** (*b*) **5.** (*a*) **6.** (*a*) **7.** (*c*) **8.** [24]
9. [4] **10.** [72] **11.** [125]

CHAPTER

5

Chemical Bonding and Molecular Structure

Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

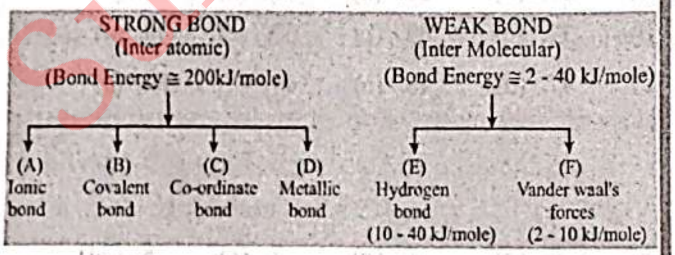
INTRODUCTION

Atoms combine with one another in different ways to form a large number of molecules. The attractive force which holds the constituents (atoms, molecules or ions) together in different chemical species, is called a **chemical bond.**

As the atomic state is regarded as a state of higher energy therefore the atoms combine with one another in a number of ways.

Key Note

- A molecule will only be formed if it is more stable and has a lower energy than the individual atoms.


STRONG BOND
(Inter atomic)
(Bond Energy ≅ 200kJ/mole)
WEAK BOND
(Inter Molecular)
(Bond Energy ≅ 2 - 40 kJ/mole)
(A) Ionic bond
(B) Covalent bond
(C) Co-ordinate bond
(D) Metallic bond
(E) Hydrogen bond (10 - 40 kJ/mole)
(F) Vander waal's forces (2 - 10 kJ/mole)

Cause of Chemical Combination

(I) Atom combines to acquire noble gas configuration.

(II) Outermost electrons participate in bond formation.

TYPES OF BONDS

1. **Electrovalent or ionic bond** (by transfer of e^- from one atom to another)
2. **Covalent bond** (by sharing of a pair of e^- between two atoms)
3. **Coordinate or dative bond** (by donation of a pair of e^- from one atom to another)

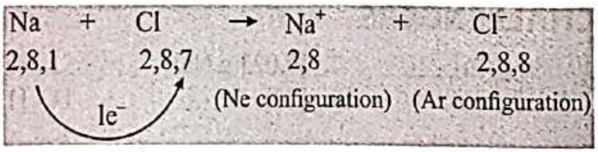
ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called **Ionic or electrovalent bond.**

(*i*) Electro +ve atom loses electron (group IA to IIIA)

(*ii*) Electro –ve atom gains electron (group VA to VIIA)

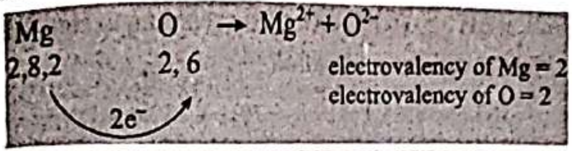
- Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.
- Strength of ionic bond ∝ Electronegativity difference
- Gr. 1 and Gr. 17 group elements form maximum ionic compounds.


Na + Cl → Na⁺ + Cl⁻
2,8,1
2,8,7
2,8
2,8,8
1e⁻
(Ne configuration)
(Ar configuration)

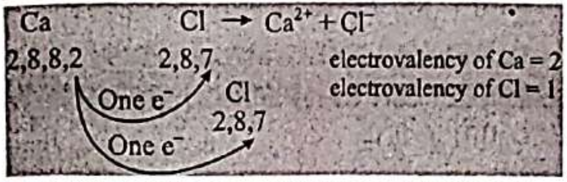
Electrovalency: It is defined as number of electrons lost or gained by an atom e.g. Na has electrovalency 1, Mg has 2.

Example:

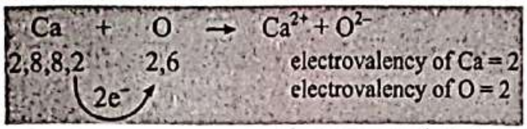
(a)



(b)



(c)



- The force of attraction is equal in all direction so ionic bond is non-directional.
- Ionic compounds do not have molecular formula. It has only empirical formula e.g. NaCl is empirical formula of sodium chloride.

CONDITIONS FOR FORMING IONIC BOND

Formation of Ionic bond depends upon these three factors

(a) **Ionisation energy:** Minimum amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation.

Lesser Ionisation energy → Greater tendency to form cation.

e.g. $\left.\begin{array}{l} Na^+ > Mg^{2+} > Al^{3+} \\ Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \end{array}\right\}$ ionic bond formation tendency

(b) **Electron affinity:** Amount of energy released when an electron is added to an isolated gaseous atom to form –ve ion (anion).

Higher electron affinity → Greater tendency to form anion

e.g. $F^- > O^{2-} > N^{3-}$ } tendency to form ionic bond

(c) **Lattice energy:** Amount of energy released when one mole of ionic solid crystal lattice is formed from its gaseous ions.

Higher lattice energy → Greater will be the stability or strength of ionic bond.

Factors affecting lattice energy (U):

(i) Magnitude of charge → $U \propto z^+ z^-$ (Ionic charge)

Lattice energy ∝ Magnitude of charge

NaF	MgF_2	AlF_3
Na^+	Mg^{+2}	Al^{+3}

$\xrightarrow{\hspace{10em}}$

– Charge of Cation increases

– Lattice energy increases

(ii) Size of ions : – Lattice energy $\propto \dfrac{1}{\text{size of ion}}$

LiF NaF KF RbF CsF

$\xrightarrow{\hspace{10em}}$

– Size of cation increases (Size of anion is constant)

– Lattice energy decreases

Note: This concludes that **for lower value of IE and higher value of EA, there is more ease of formation of the cation & anion respectively and consequently more chances of electrovalent bond formation.**

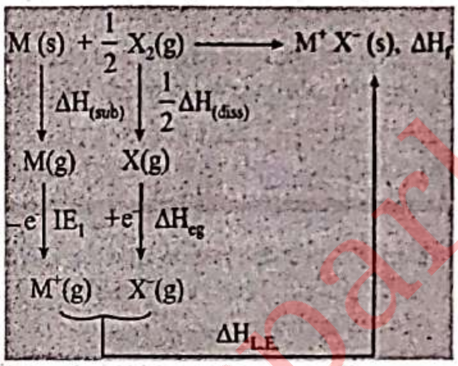
DETERMINATION OF LATTICE ENERGY

Born-Haber Cycle (Indirect Method): It inter-relates the various energy terms involved during formation of an ionic compound.

It is a thermochemical cycle based on the Hess's law of constant heat summation.

"The net enthalpy change of a chemical reaction or of any process always remain same whether the reaction takes place in one step or many steps" as given in following flow chart.

$$M(s) + \frac{1}{2}X_2(g) \longrightarrow M^+X^-(s), \Delta H_f$$



ΔH_f = heat of formation of M^+X^-

$\Delta H_{(sub)}$ = heat of sublimation of M

IE_1 = ionisation energy of M

$\Delta H_{(diss)}$ = heat of dissociation of X_2

ΔH_{eg} = electron gain enthalpy of X

$\Delta H_{L.E.}$ = Lattice energy of M^+X^-.

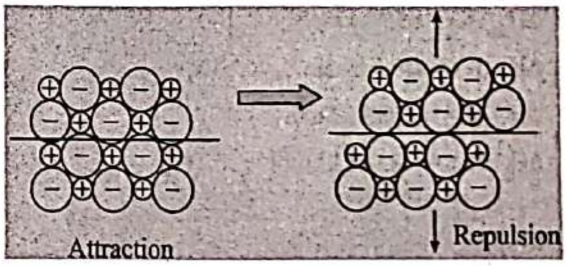
So according to Hess's law.

$$\Delta H_f = \Delta H_{(sub)} + IE_1 + \frac{1}{2}\Delta H_{(diss)} + \Delta H_{eg} + \Delta H_{L.E.}$$

PROPERTIES OF IONIC COMPOUNDS

(a) **Physical state:** Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



(b) **Boiling point and melting point:** Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(c) **Conductivity:** In solid state - No free ions hence Bad conductor of electricity.

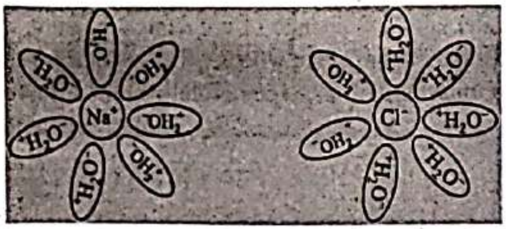
In fused state or aqueous solution - due to free ions - Good conductor of electricity.

(*d*) **Solubility:** Highly soluble in water (Polar solvents)

Example: NaCl in water

(*i*) The Na^+ ions get associated with -vely charged 'O' of water

(*ii*) And Cl^- ions associates with +vely charged 'H' of water.



(*iii*) Thus charge on Na^+ and Cl^- decreases and electrostatic force of attraction also decreases which leads to free ions.

Key Note

- The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.
- For an ionic compound to be soluble in water – Hydration energy > Lattice energy
- Hydration energy $\propto \frac{1}{r^+} + \frac{1}{r^-}$ {r^+ & r^- are radius of cation and anion}
- Hydration energy mainly depends on the cation radius because the value $\frac{1}{r^-}$ is negligible in comparison to $\frac{1}{r^+}$.
- Down the group both the lattice energy & hydration energy decreases

Train Your Brain

Example 1: Calculate the lattice energy of solid KF with the help of following data:

$\Delta H^0_f(KF) = -562.6 \text{ kJ mol}^{-1}$

$\Delta H_{sub}(K) = 89.6 \text{ kJ mol}^{-1}$

$\Delta H_{IE}(K) = 419.0 \text{ kJ mol}^{-1}$

$\Delta H_{diss}(F_2) = 158.2 \text{ kJ mol}^{-1}$

$\Delta H_{EA}(F) = -332.6 \text{ kJ mol}^{-1}$

Sol. $K(s) + \frac{1}{2}F_2(g) \longrightarrow KF(s)\ ;\ -562.6 \text{ kJ mol}^{-1}$

$K(s) \longrightarrow K(g);\ 89.6 \text{ kJ mol}^{-1}$

$K(g) \longrightarrow K^+(g) + e^-;\ 419.0 \text{ kJ mol}^{-1}$

$\frac{1}{2}F_2(g) \longrightarrow F(g);\ \frac{1}{2}(158.2) = 79.1 \text{ kJ mol}^{-1}$

$F(g) + e^- \longrightarrow F^{(-)}(g);\ -332.6 \text{ kJ mol}^{-1}$

Let $\Delta H_{lattice}$ (KF) be U, then according to Hess's law of constant heat summation.

$-562.6 = 89.6 + 419.0 + 79.1 - 332.6 + U$

So, $U = -817.7 \text{ kJ mol}^{-1}$

Lattice energy of KF $= -817.7 \text{ kJ mol}^{-1}$

Example 2: Lattice energy of $BeCO_3$ (I), $MgCO_3$ (II) and $CaCO_3$ (III) are in the order -

(*a*) I > II > III (*b*) I < II < III

(*c*) I < III < II (*d*) II < I < III

Sol. (*a*) Lattice energy $\propto \frac{1}{\text{Cation size}}$

$BeCO_3 > Mg\ CO_3 > CaCO_3$ (L.E)

L.E. decrease from top to bottom.

Example 3: Which of the following statements is wrong regarding ionic compounds?

(*a*) These are generally in solid state at room temperature.

(*b*) The force of attraction between ions is non directional.

(*c*) Ionic compounds are soluble in all solvents.

(*d*) They conduct electricity in molten and solution state.

Sol. (*c*) Ionic compound are soluble only in polar solvents.

Example 4: When two atoms combine to form a molecule

(*a*) Energy is released.

(*b*) Energy is absorbed.

(*c*) Energy is neither released nor absorbed.

(*d*) Energy may either released or absorbed.

Sol. (*a*) To attain stability energy is released.

Concept Application

1. Which of the following factors is dependent upon lattlice energy?

   (*a*) Stability of ionic compound

   (*b*) Melting point of ionic compound

   (*c*) Boiling point of ionic compound

   (*d*) All of the above

2. The electrovalency of the element is equal to the:

   (*a*) Number of electrons lost

   (*b*) Number of electrons gained

   (*c*) Number of electrons transferred

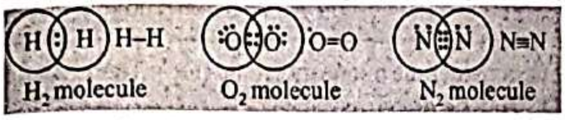
   (*d*) Number of electrons lost or gained by the atom of the element during the formation of ions of ionic compound

3. The compound which has the highest lattice energy is

   (*a*) LiF (*b*) LiCl (*c*) NaCl (*d*) MgO

COVALENT BOND

(I) A covalent bond is formed by the mutual sharing of electrons between two atoms of electronegative elements to complete their octet (Except H which completes its duplet).



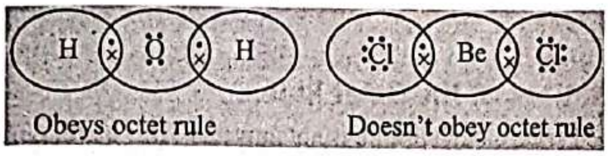
(II) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(III) Sharing of electrons may occur in three ways –

No. of electron shared between two atoms	Electron pair	Bond
2	1	Single bond (–)
4	2	Double bond (=)
6	3	Triple bond (≡)

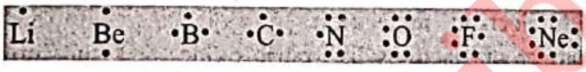
OCTET RULE

Lewis postulated that atoms achieve the stable octet (i.e. 8 electrons in their outer most shells), when they are linked by chemical bonds.



LEWIS SYMBOLS

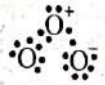
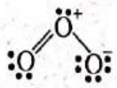
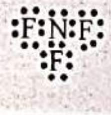
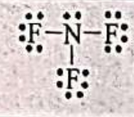
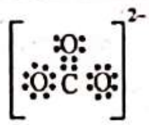
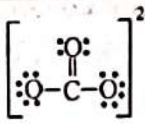
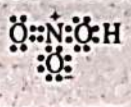
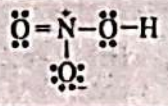
In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called as Lewis symbols. For example, the Lewis symbols for the elements of second period are as follow:



Significance of Lewis Symbols

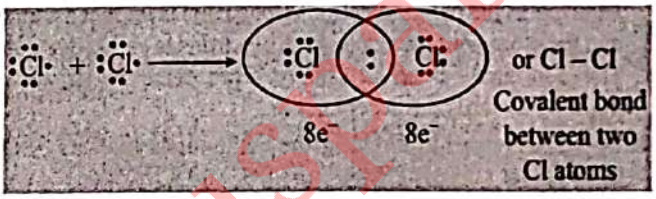
The number of dots around the symbol represents the number of valence electrons. This number of valence electrons help to calculate the common or group valence of the elements.

The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Molecule / Ion	Lewis Representation	
H_2	H : H	H – H
O_2	$:\ddot{O}::\ddot{O}:$	$:\ddot{O}=\ddot{O}:$
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

LEWIS STRUCTURE AND COVALENT BOND

The **Lewis-Langmuir theory** can be understood by considering the formation of the chlorine molecule, Cl_2. The Cl atom with electronic configuration, $[Ne]^{10}\ 3s^2\ 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process, both Chlorine atoms attain the outer most shell octet of the nearest noble gas (i.e., argon).



The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

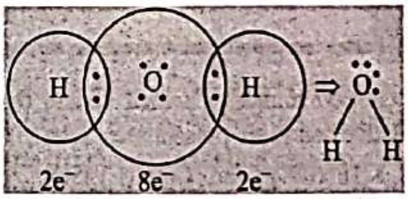
(*i*) Each bond is formed as a result of sharing of an electron pair between the atoms.

(*ii*) Each combining atom contributes at least one electron to the shared pair.

(*iii*) The combining atoms attain the outer- shell noble gas configurations as a result of the sharing of electrons.

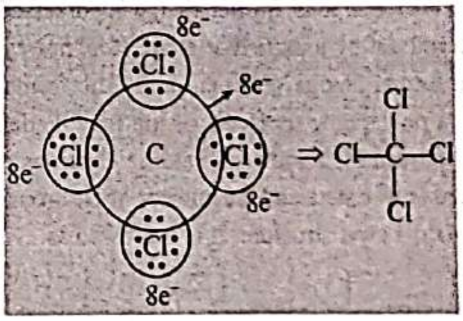
Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

(*a*)



H atoms attain a duplet of electrons and O attain the octet, here O has 2 lone pairs

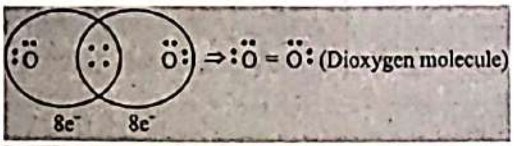
(*b*)



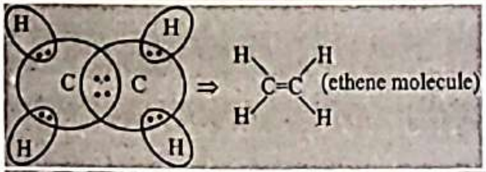
Each of the four Cl atoms along with the C atom attains octet of electrons, here each Cl atom has 3 lone pairs.

Multiple Covalent Bonds

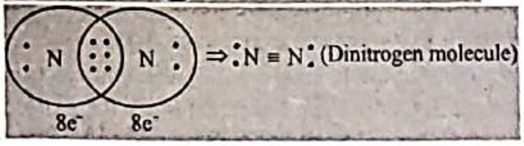
(*a*)



(*b*)

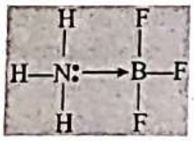


(*c*)



COORDINATE OR DATIVE BOND

- In this type of combination, both the electrons needed for sharing are contributed only by one atom. The atom which contributes the pair of electrons (lone pair) is known as donor and the atom which accepts these electrons is called acceptor. The coordinate bond is usually represented by an arrow pointing towards the acceptor. e.g.,
- Coordinate bond is found in the compounds like SO_2, SO_3, O_3, NH_4^+, H_3O^+, NH_4Cl, SO_4^{2-}, H_2SO_4 and KNO_3 etc.



Characteristics of Coordinate Compounds

- These are usually insoluble in water but soluble in organic solvents. They usually do not conduct electricity. The M.P. and B.P. of these compounds are higher than covalent compounds but lesser than the ionic compounds. The coordinate bond is directional so these compounds exhibit isomerism.

Key Note

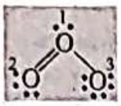
Examples of the compounds in which all the three ionic, covalent and dative bonds are present are:
$CuSO_4$, NH_4X, $K_4[Fe(CN)_6]$ and $[Cu(NH_3)_4]SO_4$

FORMAL CHARGE

In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as:

$$\boxed{\begin{array}{c}\text{Formal charge}\\ \text{(F.C.) on an atom in}\\ \text{a Lewis structure}\end{array}} = \boxed{\left[\begin{array}{c}\text{Total number of valence}\\ \text{electrons in the free atom}\end{array}\right] - \left[\begin{array}{c}\text{Total number of non bonding (lone}\\ \text{pair) electrons on that atom}\end{array}\right] - \left(\frac{1}{2}\right)\left[\begin{array}{c}\text{Total number of bonding (shared}\\ \text{electrons) around that atom}\end{array}\right]}$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3, may be drawn as:



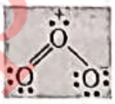
The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1 $= 6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 $= 6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 $= 6 - 6 - \frac{1}{2}(2) = -1$

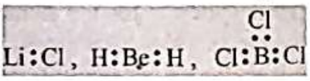
Hence, we represent O_3 along with the formal charges as follows:



Limitations of the Octet Rule

The octet rule though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

(*a*) **The incomplete octet of the central atom:** In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.



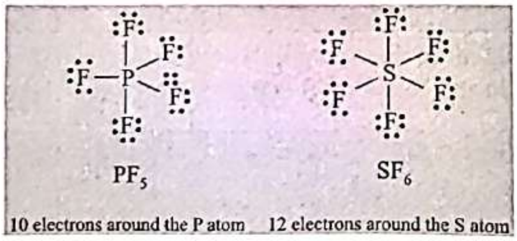
$Li{:}Cl,\ H{:}Be{:}H,\ Cl{:}\overset{Cl}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}}{:}Cl$

(*b*) **Odd-electron molecules:** In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide NO_2, the octet rule is not satisfied for all the atoms

$\ddot{N} = \ddot{O},\ \ddot{O} = \overset{+}{N} - \ddot{O}:$

(*c*) **The expanded octet:** Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements, there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

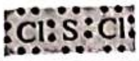
Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



10 electrons around the P atom 12 electrons around the S atom

Key Note

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



(*d*) Other drawbacks of the octet theory

(*i*) It is clear that octet rule is based upon the chemical inertness of noble gases. However, xenon (and krypton) combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , $XeOF_2$ etc.,

(*ii*) This theory does not account for the shape of molecules.

(*iii*) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Train Your Brain

Example 5: The combination of atoms occur because they want

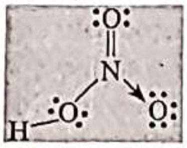
(*a*) To decrease number of electrons in the outermost orbit
(*b*) To attain an inert gas configuration or to attain stability
(*c*) To increase number of electrons in the outermost orbit
(*d*) To attain 18 electrons in the outermost orbit

Sol. (*b*) Combination of atoms occur to attain an inert gas configuration

Example 6: Which of the following contains a coordinate covalent bond?

(*a*) HNO_3 (*b*) $BaCl_2$ (*c*) HCl (*d*) H_2O

Sol. (*a*) HNO_3 contains 1 coordinate covalent bond

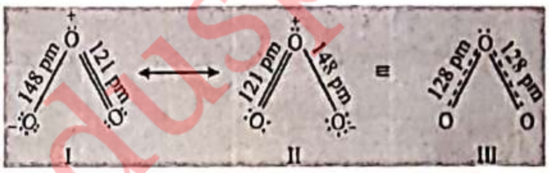


Concept Application

4. A bond formed between two like atoms cannot be
   (*a*) ionic (*b*) covalent
   (*c*) coordinate (*d*) metallic
5. To which of the following species is the octet rule applicable?
   (*a*) BrF_5 (*b*) SF_6 (*c*) IF_7 (*d*) CO_2
6. Octet configuration can be achieved through :
   (*a*) loss of electrons (*b*) gain of electrons
   (*c*) sharing of electrons (*d*) All of these
7. Which of the following species does not obey octet rule:
   (*a*) SiF_4 (*b*) PCl_5
   (*c*) ICl (*d*) BF_4^-
8. In which of the following species the bonds are Non-directional?
   (*a*) NCl_3 (*b*) RbCl (*c*) $BeCl_2$ (*d*) BCl_3
9. Which of the following molecules does not have coordinate bonds?
   (*a*) CH_3–NC (*b*) CO (*c*) O_3 (*d*) CO_3^{2-}
10. Which of the following compounds is covalent?
    (*a*) H_2 (*b*) CaO (*c*) KCl (*d*) Na_2S
11. The compound which contains both covalent and co-ordinate bond is -
    (*a*) CO (*b*) NaCl
    (*c*) H_2SO_4 (*d*) None of these

RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

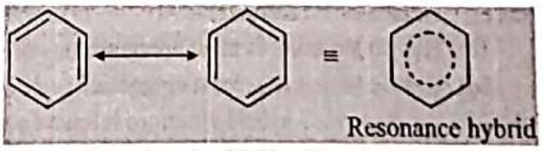


Structures I and II represent the two canonical forms while the structure III is the resonance hybrid.

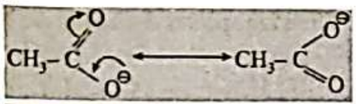
In both structures, we have O – O single bond and O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are identical (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

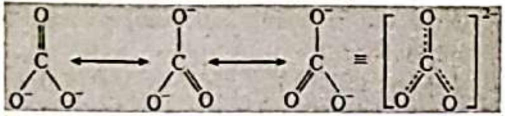
The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. According to the concept of resonance, **whenever a single Lewis structure cannot describe a molecule accurately, a number of hypothetical valid structures with (i) similar energy, (ii) identical positions of nuclei, and (iii) same number of bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid structure which describes the molecule accurately.**

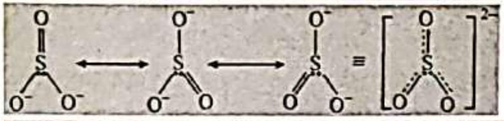
Thus for O_3, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

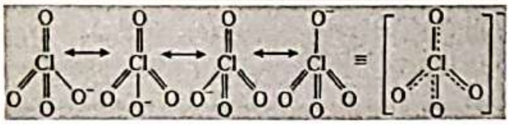


e.g.

(i)


(ii)


(iii)


(iv)


Rules of Stability Order of Resonating Structures:

(i) That structure is more stable which has more number of covalent bonds or complete octet of all atoms.

(ii) Greater charge separation means less stability. (Charged structures are less stable)

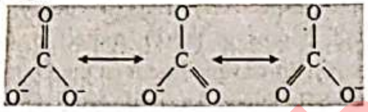
(iii) Like charges are more stable when farther and unlike charges are more stable when closer.

(iv) Positive charge is more stable on more electropositive atom and negative charge is more stable on more electronegative atom.

Key Note

- **Bond order** $= \dfrac{\text{Total No. of bonds formed between two atoms in all identical resonating structures}}{\text{Total No. of identical resonating structures}}$

  e.g.,



$$\text{Bond order} = \frac{2+1+1}{3} = 1.33$$

- Resonance energy = Energy of actual molecule (resonance hybrid) – Energy of most stable resonating structure.
- Stability of molecule α resonance energy.
- More is the number of covalent bonds in molecule, more will be its resonance energy.
- Resonance energy α number of identical resonating structures.

Train Your Brain

Example 7: What is not true about resonance?

(a) The resonating structures are hypothetical

(b) The unpaired electrons in various resonating structures are same

(c) Hybrid structure is most energetic

(d) Hybrid structure is least energetic

Sol. (d) In resonance hybrid structure is least energetic

Concept Application

12. Which of the following conditions is not correct for resonating structures?

(a) The contributing structures must have the same number of unpaired electrons

(b) The contributing structures may have different energies

(c) The contributing structures should be so written that unlike charges reside on atoms that are far apart

(d) The positive charge should be present on the electropositive element and the negative charge on the electronegative element

MODERN CONCEPT OF COVALENT BOND (VBT)

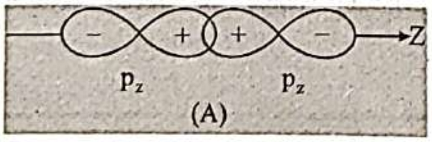
As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol^{-1}, 74 pm) and F_2 (150.6 kJ mol^{-1}, 42 pm); although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. To overcome these limitations the two Important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

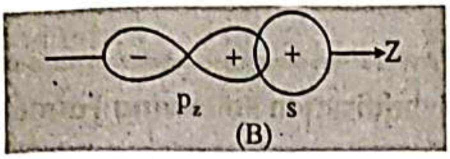
Orbital Overlap Concept: In the formation of di-hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap, the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present, in the valence shell having opposite spins.

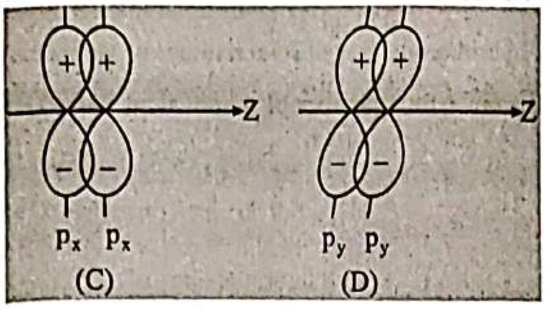
Overlapping of Atomic Orbitals: When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules.

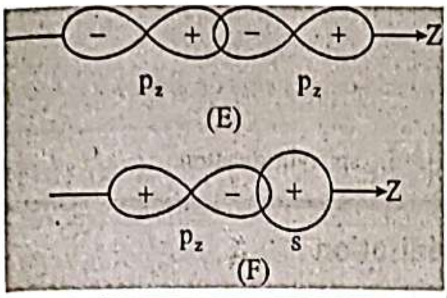
Positive overlap

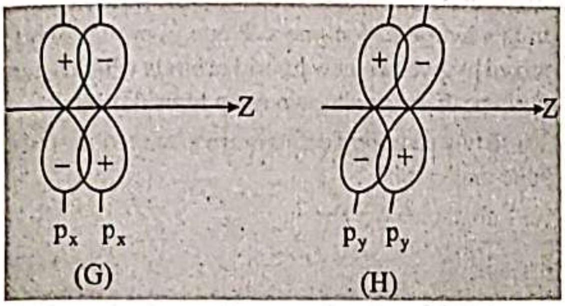




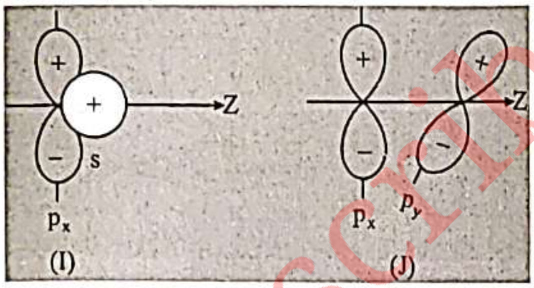


Negative overlap





Zero overlap



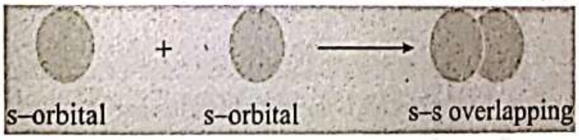
Note: s-p_y, p_x-p_z, p_y-p_z also leads to zero overlap.

Types of Overlapping and Nature of Covalent Bonds: The covalent bond may be classified into two types depending upon the types of overlapping:

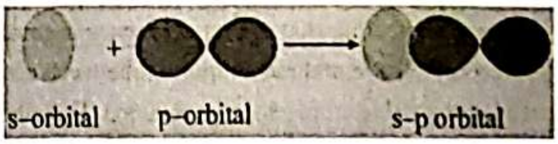
(*i*) sigma(σ) bond, and (*ii*) pi (π) bond

(*i*) **Sigma (σ) bond:** This type of covalent bond is formed by the end to end overlap of bonding orbitals along the internuclear axis. This is called as head-on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

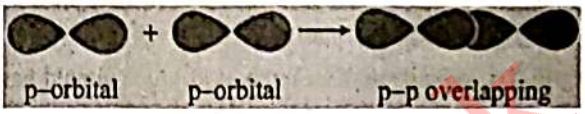
- **s-s overlapping:** In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below:



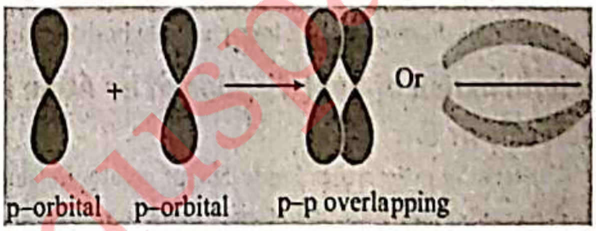
- **s-p overlapping:** This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom along the internuclear axis.



- **p-p overlapping:** This type of overlap takes place between half filled p-orbitals of the two approaching atoms along the internuclear axis.



(*ii*) **pi(π) bond:** In the formation of π bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



Strength of Sigma and pi Bonds: Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond .

σ bond strength : s - s < s - p < p - p

π bond strength : 2pπ - 2pπ > 2pπ - 3pπ > 3pπ - 3pπ

HYBRIDISATION

The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. It does not give the explanation why $BeCl_2$ is linear, BF_3 is planar, CH_4 is tetrahedral, NH_3 is pyramidal and water is V– shaped molecule.

In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling & Slater.

According to them the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals.** Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under:

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are equivalent in energy and shape.

3. The hybrid orbitals are more directional and hence more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important Conditions for Hybridisation

(*i*) The orbitals present in the valence shell of the atom are hybridised.

(*ii*) The orbitals undergoing hybridisation should have almost equal energy.

(*iii*) Promotion of electron is not essential condition prior to hybridisation.

(*iv*) It is the orbital that undergo hybridization and not the electrons. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

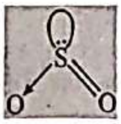
Determination of Hybridisation of an Atom in a Molecule or Ion

Steric number rule: Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) on that atom.

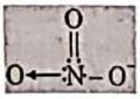
Note: This rule is not applicable to molecules/ions which have odd e^- (ClO_2, NO, NO_2), free radicals and compounds like B_2H_6 which involve 3 centre $2e^-$ bond (banana bond).

For Example :

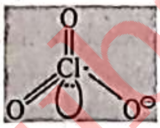
O = C = O S.No. = 2 + 0 = 2



S.No. = 2 + 1 = 3



S.No. = 3 + 0 = 3



S.No. = 3 + 1 = 4

Steric number	Types of Hybridisation	Geometry
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
7	sp^3d^3	Pentagonal bipyramidal

Key Note

To Predict Hybridisation Following Formula May be Used

No. of hybrid orbital = $\frac{1}{2}$ [Total number of valence e^- in the central atom + total number of monovalent atoms − charge on cation + charge on anion]

eg. for NH_4^+; $\frac{1}{2}$ [5 + 4 − 1] = 4, sp^3 hybridisation.

SF_4 ; $\frac{1}{2}$ [6 + 4] = 5, sp^3d hybridisation.

SO_4^{2-}; $\frac{1}{2}$ [6 + 2] = 4, sp^3 hybridisation.

('O' is divalent so add only charge on anion)

NO_3^-; $\frac{1}{2}$ [5 + 1] = 3, sp^2 hybridisation.

Types of Hybridisation

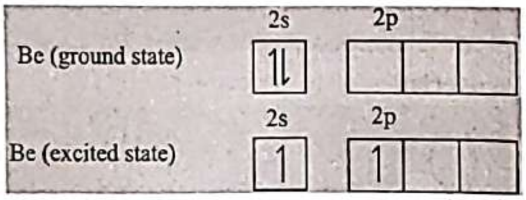
sp Hybridisation

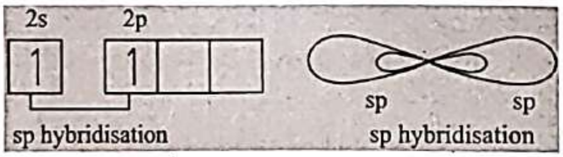
(I) In this hybridisation one s & one p–orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.

(II) These two sp hybrid orbitals are arranged in straight line at bond angle 180°.

(III) %s - character = 50%

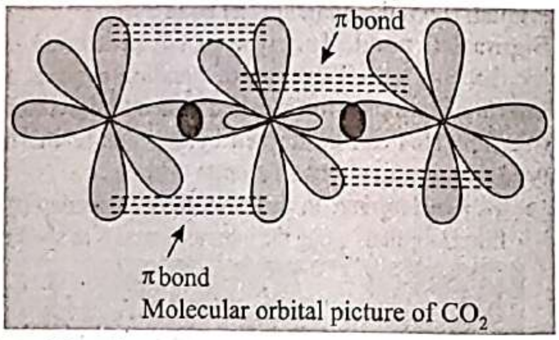
e.g.





Key Note

- **CO_2 Molecule (O = C = O):** In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



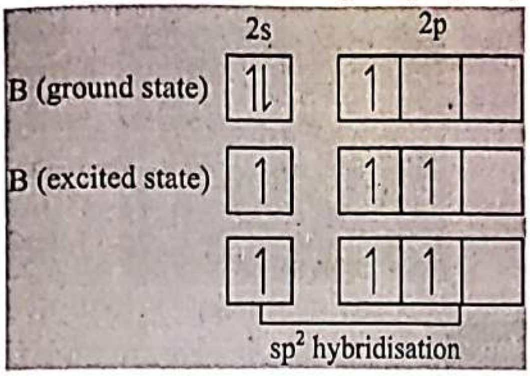
Molecular orbital picture of CO_2

- Thus, CO_2 molecule is linear in shape having 180° bond angle.

sp^2 Hybridisation

(I) In this hybridisation one s & two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are of the same shape & equivalent energies.

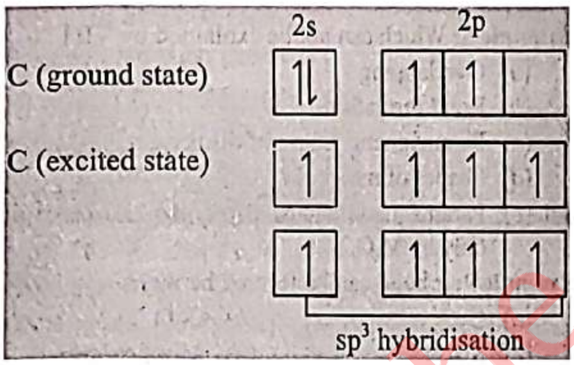
(II) These three sp^2 hybrid orbitals are at angle of 120° giving **trigonal planar shape.** e.g., BF_2, $AlCl_3$, SO_2, NO_3^-, NO_2^-, NO_2

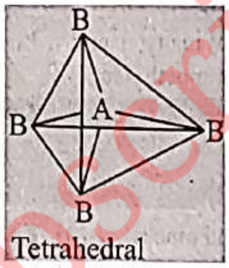

2s
2p
B (ground state)
B (excited state)
sp² hybridisation

sp^3 Hybridisation

(*i*) In this hybridisation, one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

(*ii*) The angle between these four hybrid orbitals will be 109°28.


2s
2p
C (ground state)
C (excited state)
sp³ hybridisation



Tetrahedral

The shape obtained from these hybrid orbitals would be tetrahedron.

Three following cases represent sp^3 hybridisation.

(*a*) **Four sigma bonds with zero lone pair of electron:**

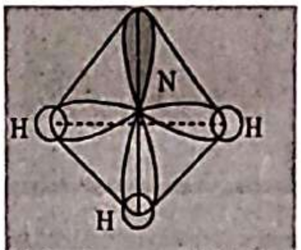
E.g., CH_4, CF_4, SiO_4^{4-}, $SiCl_4$, SO_4^{2}, PO_4^{3-}, NH_4^+, BF_4^-, AlF_4^-, BeF_4^{2-}

In above compounds, bond angle is 109°28' & tetrahedron shape.

(*b*) **Three sigma bonds & one lone pair of electron:**

E.g. NH_3, NF_3, PF_3, NCl_3, PCl_3, CH_3^- H_3O^+, ClO_3^-

Pyramidal shape & bond angle will be less than 109.5° due to the presence of the lone pair electron on nitrogen which repels bond pair electrons therefore bond angle is reduced from 109°28' to 107°. (The repulsion between ℓp – b.p > bp – bp).

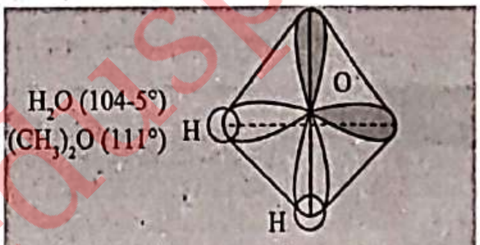


Molecular pyramidal orbital of NH_3

(*c*) **Two sigma bonds & two lone pair of electrons:**

E.g., H_2O, OCl_2, OBr_2, OF_2, OI_2 etc.

Angular shape and bond angle will be either less then 109°28' or more than 109°28'.

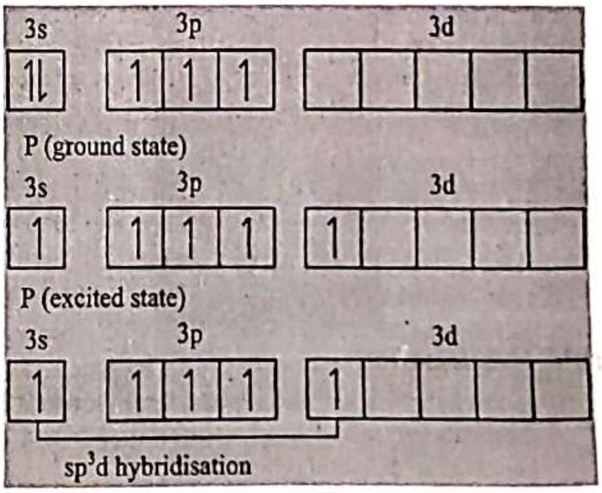

O
H₂O (104·5°)
(CH₃)₂O (111°)
H
H

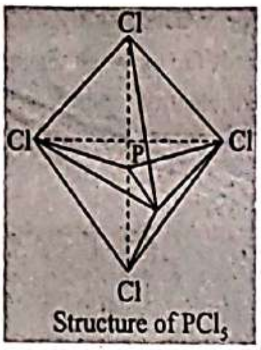
Molecular angular orbital of H_2O

sp^3d Hybridisation

(*i*) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals called as sp^3d hybrid orbitals.

(*ii*) Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes trigonal bipyramidal. e.g., PF_5, I_3^-, ICl_2^-, PCl_5, AsF_5, SF_4, $SbCl_5$, ClF_3 etc.


3s
3p
3d
P (ground state)
3s
3p
3d
P (excited state)
3s
3p
3d
sp³d hybridisation



Structure of PCl_5

Key Note

In sp^3d hybridisation, d_{z^2} orbital is hybridised with s and p orbitals.

sp^3d^2 Hybridisation

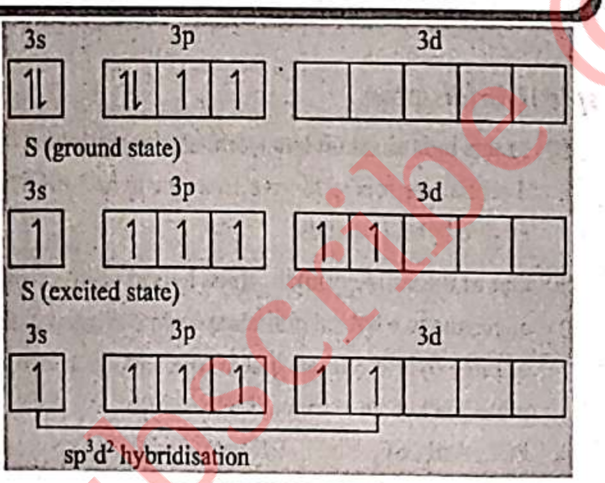
(*i*) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.

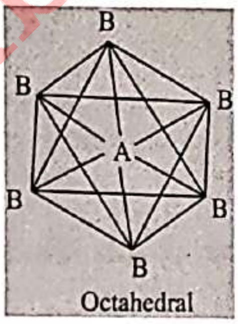
(*ii*) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.

(*iii*) The angle between all hybrid orbitals will be 90° or 180°.
eg., SF_6, AlF_6^{3-}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,

Key Note

Two 'd' orbital participating in sp^3d^2 hybridisation are $d_{x^2-y^2}$ and d_{z^2}.





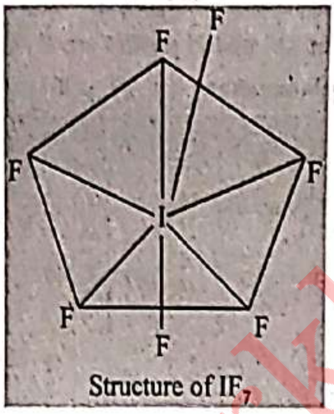
Octahedral

sp^3d^3 Hybridisation

(*i*) In this hybridisation, one s-orbital three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.

(*ii*) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.

(*iii*) Five bond angles are of 72° & ten bond angles of 90°.
e.g., IF_7 & XeF_6.



Structure of IF_7

Key Note

In sp^3d^3 hybridisation, d-orbitals generally involved are d_{xy}, d_{z^2} & $d_{x^2-y^2}$ orbitals.

Train Your Brain

Example 8: Which can not be explained by VBT?

(*a*) Overlapping
(*b*) Bond formation
(*c*) Paramagnetic nature of di-oxygen
(*d*) Shapes of molecules

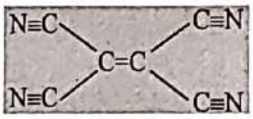
Sol. (*c*) Paramagnetic nature of oxygen can be explained only by M.O.T

Example 9: π bond can be formed between

(*a*) C–C
(*b*) O–O
(*c*) N – N
(*d*) All of these

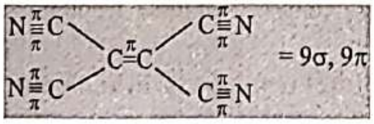
Sol. (*d*) All of these

Example 10: How many σ and π bonds are there in the molecule of tetracyanoethylene?



(*a*) Nine σ and nine π
(*b*) Five σ and nine π
(*c*) Nine σ and seven π
(*d*) Five σ and eight π

Sol. (*a*)



Example 11: The relative overlap of orbitals decreases in the order

(*a*) $sp > sp^2 > sp^3 >> p$
(*b*) $sp^3 > sp^2 > sp >> p$
(*c*) $p > sp^3 > sp^2 > sp$
(*d*) $p > sp > sp^2 > sp^3$

Sol. (*a*) $sp > sp^2 > sp^3 >> p$

Example 12: The hybridization of carbon atoms in $\dot{C}-\dot{C}$ single bond of $H-C\equiv C-CH=CH_2$ is

(*a*) sp^3-sp^3 (*b*) sp^2-sp

(*c*) sp^2-sp^2 (*d*) sp^3-sp

Sol. (*b*) sp^2-sp

Example 13: Which of the following is not true for a hybridisation process?

(*a*) Electrons take part and not the orbitals

(*b*) Participating orbitals have almost equal energy

(*c*) Hybrid orbitals have identical shape

(*d*) Hybrid orbitals have identical energies

Sol. (*a*) Electrons do not take part in hybridization.

Example 14: Choose the molecules in which hybridisation occurs in the ground state-

(i) BCl_3 (ii) NH_3 (iii) PCl_3 (iv) BeF_2

The correct answer is

(*a*) i, ii, iv (*b*) i, ii, iii

(*c*) ii, iii (*d*) iii, iv

Sol. (*c*) NH_3 and PCl_3 have G.S hybridization.

Example 15: Which of the following is not correct statement?

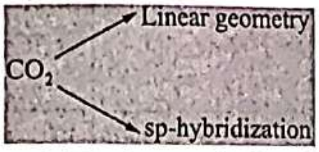
(*a*) CO_2, Irregular geometry

(*b*) BF_3, Regular geometry

(*c*) NH_3, Irregular geometry

(*d*) SO_2, Irregular geometry

Sol. (*a*)

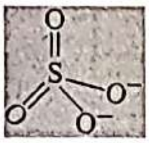


Example 16: The shape of sulphate ion is

(*a*) hexagonal (*b*) square planar

(*c*) trigonal bipyramidal (*d*) tetrahedral

Sol. (*d*)



so structure is tetrahedral.

Example 17: Among NO_3^-, CO_3^{2-}, ClO_3^-, SO_3^{2-}, AsO_3^- and BO_3^- the non-planar species are

(*a*) CO_3^{2-}, SO_3^{2-}, BO_3^- (*b*) AsO_3^-, ClO_3^-, SO_3^{2-}

(*c*) NO_3^-, CO_3^{2-}, BO_3^- (*d*) NO_3^-, SO_3^{2-}, BO_3^-

Sol. (*b*) AsO_3^-, ClO_3^-, SO_3^{2-}, are sp^3 hybridised so structure are tetrahedral

Concept Application

13. Specify the hybridisations of central atom in the following species respectively {N_3^-, NOCl, N_2O}

(*a*) sp , sp^2 , sp (*b*) sp , sp , sp^3

(*c*) sp^2 , sp , sp (*d*) sp^2 , sp^2 , sp.

14. Which of the following has a geometry different from the other three species (having the same geometry)?

(*a*) BF_4^- (*b*) SO_4^{2-} (*c*) XeF_4 (*d*) PH_4^+

15. Which of the following species given below have shape similar to $XeOF_4$?

(*a*) XeO_3 (*b*) IOF_4^+ (*c*) PCl_5 (*d*) $XeF_5^{\oplus}$

16. The number of π bonds and σ-bonds in case of lewis structure of SO_4^{2-} are:

(*a*) 4σ, 2π (*b*) 4σ, 1π

(*c*) 4σ, zero π (*d*) 4σ, 4π

17. Indicate the wrong statement according to Valence bond theory

(*a*) A sigma bond is stronger than π-bond

(*b*) p-orbitals always have only sidewise overlapping

(*c*) s-orbitals never form π-bonds

(*d*) There can be only one sigma bond between two atoms

18. A sigma bond is formed by the overlapping of

(*a*) s-s orbitals alone

(*b*) s and p orbitals alone

(*c*) s–s, s–p or p–p orbitals along internuclear axis

(*d*) p–p orbitals along the sides

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis concept is unable to explain the shapes of molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957). This theory provides a simple procedure to predict the shapes of covalent molecules.

The Main Postulates of VSEPR Theory are as follows:

(*i*) The shape of a molecule depends upon the arrangement of valence shell electron pairs [bonded or non-bonded) around the central atom.

(*ii*) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

(*iii*) These pairs of electrons tends to occupy such positions in space that minimise repulsion and thus maximise distance between them.

(*iv*) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

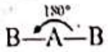
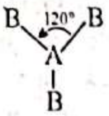
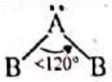
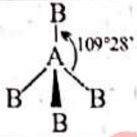
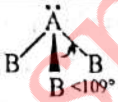
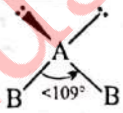
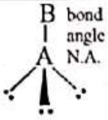
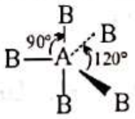
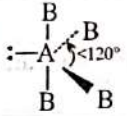
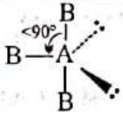
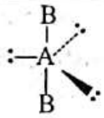
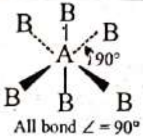
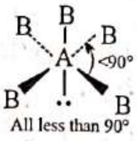
(*v*) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

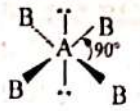
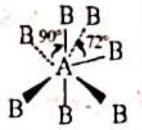
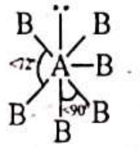
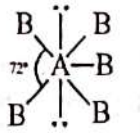
(*vi*) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order:

lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) -bond pair (bp).

Shapes of Molecules Based on VSEPR Theory

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. l_p	General formula	Type of hybridisation	Stereo chemical formula/str.	Shape	Exam.
2	2	0	AB_2	sp		linear	$BeCl_2$, NO_2^+, CO_2
3	3	0	AB_3	sp^2		Trigonal planar	BCl_3, NO_3^- GaF_3, CO_3^{2-}
3	2	1	AB_2L	sp^2		V-shape or Bent or angular	$SnCl_2$, O_3,SO_2
4	4	0	AB_4	sp^3		Tetrahedron	CH_4, SiF_4, $\overset{+}{N}H_4$
4	3	1	AB_3L	sp^3		Trigonal pyramidal	NH_3, CH_3^-
4	2	2	AB_2L_2	sp^3		V-shape or Bent or angular	H_2O, SF_2
4	1	3	ABL_3	sp^3		linear	ClO^-
5	5	0	AB_5	sp^3d		Trigonal bipyramidal	PF_5, SF_5^+, $SbBr_5$, XeO_3F_2
5	4	1	AB_4L	sp^3d		See-saw	SF_4, ICl_4^-
5	3	2	AB_3L_2	sp^3d		T-shape	ClF_3, BrF_3
5	2	3	AB_2L_3	sp^3d		Linear	ICl_2^-, XeF_2, I_3^-
6	6	0	AB_6	sp^3d^2		Octahedral or Square bipyramidal	SF_6, IF_6^+, PCl_6^-
6	5	1	AB_5L	sp^3d^2		Square pyramidal	IF_5, $XeOF_4$, BrF_5, XeF_5^+

6	4	2	AB_4L_2	sp^3d^2		Square planar	IF_4^-, XeF_4, ICl_4^-
7	7	0	AB_7	sp^3d^3		Pentagonal bipyramidal	IF_7
7	6	1	AB_6L	sp^3d^3		Distorted octahedral	XeF_6, IF_6^-
7	5	2	AB_5L_2	sp^3d^3		Pentagonal planar	XeF_5^-

HYBRIDISATION IN IONIC SOLID SPECIES

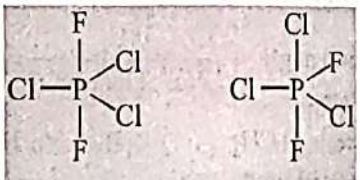
Species	Cationic part	Anionic part
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
$N_2O_3(s)$	NO^+	NO_2^- (sp^2)
I_2Cl_6 (liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
I_2(liquid)	I_3^+ (sp^3)	I_3^- (sp^3d)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)

BENT'S RULE

(*i*) A lone pair of electron prefers to occupy those hybrid orbitals which has greater percentage of s-character.

(*ii*) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

e.g., Draw the geometry of PCl_3F_2



Correct Structure

Wrong Structure

Key Note

In TBP, more electronegative atom prefers to occupy axial position whereas lone pairs or multiple bond pairs prefer equatorial positions. (axial position has smaller percentage of s-character).

DRAGO'S RULE

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

(*i*) Central atom belongs to third or lower period in periodic table

(*ii*) Central atom must contain atleast one lone pair of electron.

(*iii*) Electronegativity of surrounding atom is ≤ 2.5

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactorily if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals from central atom.

In such molecules bond angle is approximately 90°

Group 15	Bond angle	Group 16	Bond angle
NH_3	107°48'	H_2O	104°28'
PH_3	93°36'	H_2S	92°
AsH_3	91°48'	H_2Se	91°
SbH_3	91°18'	H_2Te	90.5°

❖ Correct order of bond angle.

(*a*) $H_2O > H_2S > H_2Se > H_2Te$

(*b*) $NH_3 > PH_3 > AsH_3 > SbH_3$

MOLECULES THAT DO NOT EXIST

(1) SF_4, SF_6 & PF_5 exist while OF_4, OF_6, NF_5 do not exist.

(2) (*a*) PI_5(vap) & SCl_6 do not exist while $TeCl_6$ exist.

(*b*) PI_5 (Solid) does exist.

(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist.

Determination of number of $p\pi$-$d\pi$ bonds:

Count the sum of total number of sigma bonds + lone pairs at given bonded atom = x (say).

Case I:

If "x" is less than 4 and there are "y" π-bonds present at given atom then Number of $p\pi$–$p\pi$ bonds = $(4 - x)$

Whereas Number of $p\pi$–$d\pi$ bonds = $y - (4 - x)$

Case II:

If sum is greater than or equal to 4 and there are π-bonds present at given atom then all π-bonds are of type $p\pi$-$d\pi$ bonds.

For example, SO_3 has one $p\pi$–$p\pi$ bond and one $p\pi$-$d\pi$ bond.
$(CO_3)^{2-}$ has one $p\pi$–$p\pi$ bond only.
$HClO_4$ has three $p\pi$–$d\pi$ bonds.

BOND PARAMETERS

(I) Bond order
(II) Bond Length (Bond distance)
(III) Bond Angle
(IV) Bond Energy

(I) Bond order:

In Lewis description of a covalent bond, the number of bonds between two bonded atoms in given molecule is called bond order.

For example, bond order of H_2, O_2 and N_2 are 1,2 and 3 respectively.

Also, bond order of C-O bonds in CO and CO_2 are 3 and 2 respectively.

(II) Bond Length: The average distance between the nucleus of two bonded atoms is known as bond length, normally it is represented in Å. eg. A——B

Case I: Electronegativity difference is zero then

Bond length = $d_{A-B} = r_A + r_B$

where r_A and r_B are covalent radius of A & B respectively.

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

Case II: Electronegativity difference is not equal to zero then

Bond length is given by Schomaker & Stevenson formula:

Bond length = $r_A + r_B - 0.09\,(X_A - X_B)$

X_A and X_B are electronegativity of A & B respectively.

Factors affecting Bond Length:

(*a*) Electronegativity:

$$\text{Bond lengh} \propto \frac{1}{\Delta EN}$$

H-F < H-Cl < H-Br < H-I (Bond length order)

(*b*) Bond order or number of bonds:

$$\text{Bond length} \propto \frac{1}{\text{Number of bonds or bond order}}$$

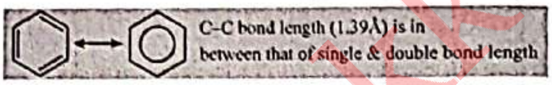
e.g. C–C, C = C, C ≡ C

1.54 Å 1.34 Å 1.20 Å (Bond length)

$\xleftarrow{\text{increasing}}$

(*c*) Resonance: (due to resonance, bond length is affected)

eg.(i) Benzene



C-C bond length (1.39Å) is in between that of single & double bond length

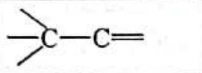
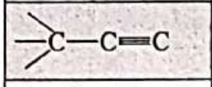
(ii) Bond length of C—O in CO_2 is 1.15 Å (in between that of double & triple bond length)

Resonance occurs in CO_2 as follows:

$$O=C=O \longleftrightarrow O^-—C\equiv O^+ \longleftrightarrow O^+\equiv C—O^-$$

(*d*) Hybridisation:

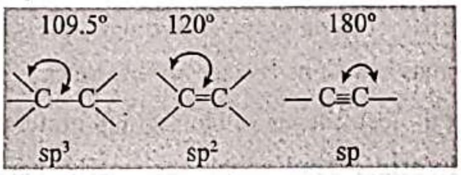
$$\text{Bond length} \propto \frac{1}{\text{s}-\text{character}}$$

Example:	Compound	Hybridisation	Bond length C—C
S-character increases ↓	Ethane	sp^3—sp^3	1.54 Å
		sp^3—sp^2	1.51 Å
		sp^3—sp	1.47 Å
	C=C—C=C	sp^2—sp^2	1.46 Å
	C=C—C≡C	sp^2—sp	1.42 Å
	C≡C—C≡C	sp—sp	1.37 Å

(III) Bond Angle: The angle between any two adjacent atoms is known as bond angle.

Factors affecting the bond angle-

(*a*) Hybridisation:



Case-I: When hybridisation is same and bonded atoms are same but central atom are from same period and no. of lone pair are different.

$$\text{Then bond angle} \propto \frac{1}{\text{No. of lone pair}}$$

Example:	CH_4	$\ddot{N}H_3$	$H_2\ddot{O}$
Hybridisation	sp^3	sp^3	sp^3
Bond angle	109°28' >	107° >	104.5°

Case-II: When hybridisation is same, bonded atoms are same and no. of lone pair is same but central atom are from same group.

Then bond angle ∝ electronegativity of central atom

Example: $\ddot{N}H_3$ $\quad \ddot{P}H_3$ $\quad \ddot{A}sH_3$

Bond angle 107° 93° 91°

$$\xrightarrow{\hspace{6cm}}$$

– Electronegativity decreasing

– Bond angle will decrease

Case-III: When hybridisation is same, no. of lone pair is same and Central atom is same but bonded atoms are different.

sp^3 OF_2 103° – 105°

sp^3 Cl_2O 109° – 111°

sp^3 Br_2O 116° – 118° $\downarrow$ Electronegativity of bonded atom is decreasing

$$\text{Bond angle} \propto \text{size of surrounding atom} \propto \frac{1}{\text{electronegativity of surrounding atom}}$$

(IV) Bond Energy (BE): Bond energy may be defined as-

(*a*) **Bond formation energy:** Energy released when any bond is formed in gas phase is known as bond formation energy.

(*b*) **Bond dissociation energy:** Energy required to dissociate any bond is gas phase is known as bond dissociation energy.

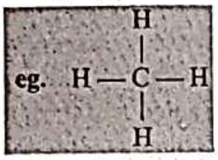
Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy.

Case-I: In diatomic molecule:

Bond energy = bond dissociation energy

eg. $N_2 > O_2 > H_2 > F_2$ (B.E. order)

Case-II: For polyatomic molecule:



Theoretical values of bond dissociation energy (d) of individual C—H bonds in CH_4 are given below-

D (CH_3—H) = 102 kcal/mole

D (CH_2—H) = 105 kcal/mole

D (CH—H) = 108 kcal/mole

D (C—H) = 83 kcal/mole

Hence average bond energy per C—H bond in methane

$$= \frac{398}{4} = 99.5 \text{ kcal/mole.}$$

Factors Affecting the Bond Energy

(*a*) Δ E.N. (*b*) Bond order

(*c*) Atomic size/radius (*d*) Bond polarity

(*e*) Resonance (*f*) Hybridisation

(*g*) Lone pair of electron

(*a*) **Δ E.N. :** Bond energy ∝ΔEN

eg. HF > HCl > HBr > HI (B.E. order)

(*b*) **Bond order:** Bond energy ∝ Bond order

eg. C—C < C = C < C ≡ C

79 143.3 199.0 (kcal/mol)

(*c*) **Atomic size/radius:** Bond energy $\propto \frac{1}{\text{Atomic size}}$

eg. C≡C < C≡N < N≡N

Key Note

Exception: In case of halogen group, order of bond energy is Cl — Cl > Br — Br > F — F > I — I

Because of higher electron density and small size of F atoms, repulsion between two F atoms weakens the bond.

Similarly S – S > O – O

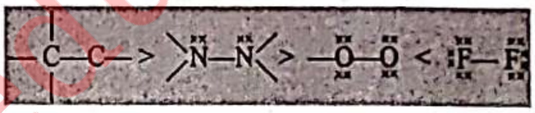
Whereas C – C > Si – Si > Ge – Ge } (B.E. order)

(*d*) **Hybridisation:** Bond energy ∝ s-character in hybrid orbitals.

eg. sp—sp > sp^2—sp^2 > sp^3—sp^3 (B.E. order)

(*e*) **Lone pair of electrons:**

$$\text{Bond energy} \propto \frac{1}{\text{lone pair of electrons}}$$

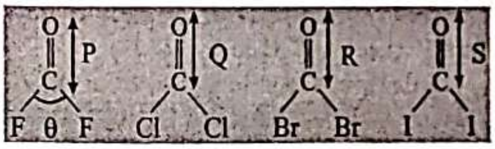


Size of F and O atoms is small so their bond energy should be high (small atomic radius) but it is actually less due to lone pair of electrons present on F and O atoms, which repel each other in F—F and —O—O— type of bonds.

Train Your Brain

Example 18: Discuss the bond angle in carbonyl halides COF_2, $COCl_2$, $COBr_2$, COI_2

Sol.

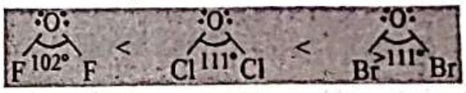


Bond angle θ ⇒ COF_2 < $COCl_2$ < $COBr_2$ < COI_2

Double bonds require more space than single bonds. Hence C = O group compresses the molecule and bond angle decrease to maximum in COF_2 as bond pairs of electrons are more closer to the fluorine atoms because of high electronegativity of fluorine. As size of halogen atoms increases and their electronegativity decreases repulsion between bond pairs increases and therefore θ increases.

Example 19: Compare bond angle of OF_2, Cl_2O and Br_2O.

Sol.



Bond pairs of electrons are more closer to the fluorine atoms (because of high electronegativity of fluorine). Also the ℓp - ℓp repulsion is more than bp - bp. Thus the F—O—F bond angle decreases to 102° from 109.5°. In Cl_2O, the bond pair are more closer to the oxygen atom because of the high electronegativity of oxygen. So the bp - bp repulsion is more than ℓp - ℓp. Thus the bond angle Cl—O—Cl increases to ≈111° due to bp - bp repulsion and repulsion between larger Cl atoms. The steric crowding of the larger halogen atoms also contributes in the increasing bond angles.

Example 20. The correct order of bond length is:

(*a*) F–F > Cl–Cl > Br–Br > I–I

(*b*) I–I > Br–Br > Cl–Cl > F–F

(*c*) Cl–Cl > Br–Br > F–F > I–I

(*d*) Br–Br > Cl–Cl > F–F > I–I

Sol. (*b*) I has largest atomic size. So, bond length of I–I is largest.

Concept Application

19. Select the correct statement

(*a*) C–O bond length of CO molecule is greater than the C–O bond length of CO_2

(*b*) C–O bond length of CO molecule is lesser than the C–O bond length of CO_2

(*c*) N–O bond length of NO_3^- ion is same as N–O bond length of NO_2^-

(*d*) N–O bond length of NO_3^- ion is lesser than the N–O bond length of NO_2^-

20. Which of the following bond angle order is incorrect?

(*a*) $NH_3 > PH_3$

(*b*) $BF_3 < PF_3$

(*c*) $O(CH_3)_2 < O(C_2H_5)_2$

(*d*) $CO_3^{2-} < CO_2$

21. Correct order of bond energy of C–O bond is

(*a*) $CO_3^{2-} > CO_2 > CO$

(*b*) $CO_2 > CO > CO_3^{2-}$

(*c*) $CO > CO_2 > CO_3^{2-}$

(*d*) None of these

22. The correct order of decreasing X – O – X bond angle is (X=H, F or Cl)

(*a*) $H_2O > Cl_2O > F_2O$

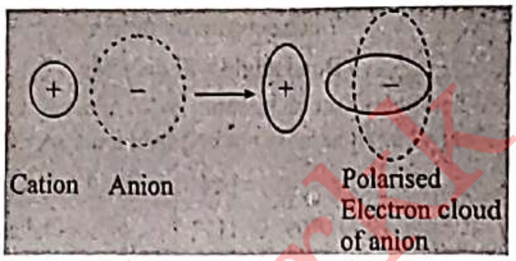
(*b*) $Cl_2O > H_2O > F_2O$

(*c*) $F_2O > Cl_2O > H_2O$

(*d*) $F_2O > H_2O > Cl_2O$

COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE)

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a nearby anion is called as polarizing power of cation.



More distortion of anion, more will be polarisation then greater is the covalent character.

Fajan's gave some rules which govern the covalent character in the ionic compounds.

(*i*) **Size of cation:** Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.

e.g. $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Size of cation increases

– Covalent character decreases

(*ii*) **Size of anion:** Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.

e.g., LiF LiCl LiBr LiI

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Size of anion increases

– Covalent character increases

(*iii*) **Charge on ion:** Higher is the charge of cation or anion, more will be the deformation of anion and thus, more will be the covalent character in compound.

Charge on cation α polarisation.

e.g., NaCl $MgCl_2$ $AlCl_3$

Na^+ Mg^{2+} Al^{3+}

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Charge of cation increases

– Covalent character increases

Charge on anion α polarisation.

e.g., AlF_3 Al_2O_3 AlN

F^-, O^{2-}, N^{3-}

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Charge on anion increases

– Covalent character increases

(iv) **Pseudo inert gas configuration of cation:** Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration cation will be more ionic whereas CuCl having pseudo inert gas configuration of cation will be more covalent in nature.

$Cu^+ = [Ne]3s^2 3p^6 3d^{10}$: $18e^-$ (Pseudo inert gas configuration)

(poor shielding of d-electrons)

$Na^+ = 1s^2 2s^2 2p^6$: $8e^-$ (Inert gas configuration)

(more shielding of s and p electrons)

Application & Exceptions of Fajan's Rule

(i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.

(ii) $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus due to greater charge, $Fe(OH)_3$ is more covalent than $Fe(OH)_2$.

(iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions. The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

For example: AgCl is white whereas AgBr, AgI, Ag_2CO_3 are yellow. Similarly, $SnCl_2$ is white but SnI_2 is black. $PbCl_2$ is white but PbI_2 is yellow.

FACTORS AFFECTING SOLUBILITY

(I) Dielectric constant: The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by "ε"

(a) Water has high value of dielectric constant ($\varepsilon = 80$)

(CH_3OH, $\varepsilon = 35$) , (Acetone, $\varepsilon = 21$)

(C_2H_5OH, $\varepsilon = 27$) , (Ether, $\varepsilon = 4.1$)

(Benzene, $\varepsilon = 2.3$)

$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$ (order of ε)

(b) Ionic compounds are more soluble in the polar solvents having high dielectric constant.

(c) H_2SO_4 and H_2O_2 have high dielectric constant but these are not good solvents due to their oxidising nature.

(II) Polarisation of anion:

$$\text{solubility} \propto \frac{1}{\text{polarisation}}$$

$$AgF > AgCl > AgBr > AgI$$
$$\xrightarrow{\qquad\qquad\qquad}$$

– Polarisation increases.

– Covalent character increases.

– Solubility decreases.

Train Your Brain

Example 21: AgCl is colourless whereas AgI is yellow, because of:

(a) Ag^+ have 18 electron in valence shell to effectively screen the nuclear charge.

(b) Ag^+ has pseudo inert gas configuration.

(c) distortion of I^- is more pronounced than Cl^- ion.

(d) existence of d – d transition.

Sol. *(c)* The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

Example 22: Compound with maximum ionic character is formed from

(a) Na and Cl *(b)* Cs and F

(c) Cs and I *(d)* Na and F

Sol. *(b)* Using fajan's rule, larger cation and smaller anion will have maximum Ionic character.

Example 23: Among the following, which one has least value of melting point?

(a) LiCl *(b)* $BeCl_2$

(c) $MgCl_2$ *(d)* $CaCl_2$

Sol. *(b)* $BeCl_2$ has maximum covalent character due to small size of Be^{2+},

Higher the covalent character, lower will be its melting point.

Example 24: Out of following which one has maximum ionic character?

(a) NaCl *(b)* KCl

(c) $CaCl_2$ *(d)* $MgCl_2$

Sol. *(b)* Due to larger size of Potassium it has least degree of polarization so it has maximum ionic character.

Example 25: Which of the following has highest melting point?

(a) NaCl *(b)* NaI

(c) NaBr *(d)* NaF

Sol. *(d)* Due to small size of Fluorine anion, it has least polarisation power so NaF has maximum ionic character. i.e, highest melting point.

Concept Application

23. Which of the following combination of ion will have highest polarisation?

(a) Fe^{2+}, Br^- *(b)* Ni^{4+}, Br^-

(c) Ni^{2+}, Br^- *(d)* Fe, Br^-

24. The correct order of decreasing polarizability of ion is:

(a) Cl^-, Br^-, I^-, F^- *(b)* F^-, I^-, Br^-, Cl^-

(c) I^-, Br^-, Cl^-, F^- *(d)* F^-, Cl^-, Br^-, I^-

25. Which of the following is correct order of increasing covalent character?

(*a*) $CCl_4 < BeCl_2 < BCl3 < LiCl$

(*b*) $LiCl < CCl_4 < BeCl_2 < BCl_3$

(*c*) $LiCl < BeCl_2 < BCl_3 < CCl_4$

(*d*) $LiCl < BeCl_2 < CCl_4 < BCl_3$

26. Which one of the following shows correct order of covalent character?

(*a*) $ZnO < ZnS$ (*b*) $ZnS = ZnO$

(*c*) $ZnS < ZnO$ (*d*) None of these

DIPOLE MOMENT (POLARITY OF BONDS)

In reality, no bond or a compound is either completely covalent or ionic.

When a covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2 the shared pair of electrons is equally attracted by the atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this, in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

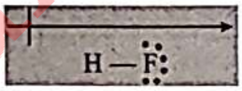
As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between the two atoms.

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (d). The conversion factors are

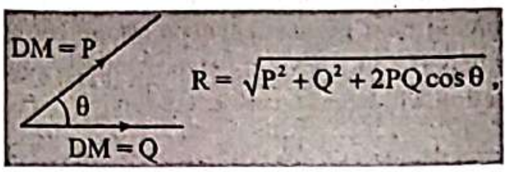
- ❖ $1\ D = 3.33564 \times 10^{-30}$ cm,
- ❖ 1 Debye $= 1 \times 10^{-18}$ e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow ($\longrightarrow$) above the Lewis structure to indicate the direction of the shift.

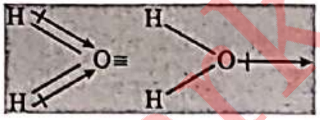
In case of polyatomic molecules, the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, **the dipole moment of a molecule is the vector sum of the dipole moments of various bonds.** i.e. a molecule will have a dipole moment if the vector summation of all of the individual bond moments is non-zero.



$$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$$

where R is the magnitude of resultant dipole moment.

For example, in H_2O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} Cm is the resultant of the dipole moments of two O—H bonds.



Net Dipole moment, $\mu = 1.85\ D = 1.85 \times 3.33564 \times 10^{-30}$ Cm $= 6.17 \times 10^{-30}$ Cm.

❖ **Following compounds have zero dipole moment:**

BF_3, CO_2, SO_3, CF_4, PF_5 (g), SF_6, XeF_2, CS_2, CCl_4, PCl_5 (g), XeF_4

Key Note

(*a*) $HF > HCl > HBr > HI$

(*b*) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

(*c*) $HF < H_2O > NH_3 > NF_3$

(*d*) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(*e*) $HF < H_2O > SO_2 > NH_3$

(*f*) $H_2O > H_2S$

(*g*) $BF_3 < NF_3 < NH_3$

(*h*) $PH_3 < PCl_3$

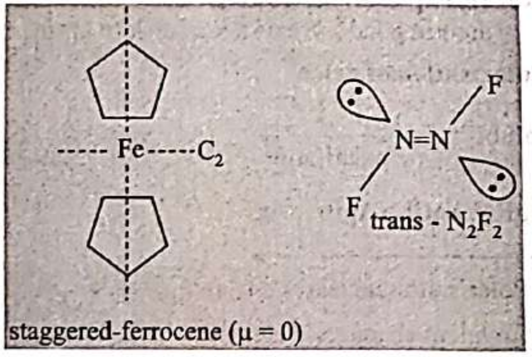
(*i*) $H_2O < H_2O_2$

(order of DM)

Key Note

❖ The presence of a centre of symmetry, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule.

Thus $[CoF_6]^{3-}$, trans – N_2F_2 and the staggered conformer of ferrocene do not have dipole moments.



APPLICATION OF DIPOLE MOMENT

(I) To determine polarity and geometry of molecule:

- A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B - F bonds are polar in BF_3 but BF_3 has $\mu = 0$ due to its symmetrical geometry.
- If molecule have $\mu = 0$, the compound is non polar and it should be linear or having symmetrical geometry.

  e.g. linear: CO_2, CS_2, $BeCl_2$ (g) ;

  symmetrical geometry – BF_3, CH_4, PCl_5, SF_6, IF_7, XeF_4.
- If molecule has $\mu \neq 0$, compound will be polar and it should be angular or having unsymmetrical geometry.

  $SnCl_2$, $PbCl_2$, SO_2: angular molecular geometry.

  NH_3, NF_3, SF_4, CH_3Cl, $CHCl_3$: unsymmetrical molecular geometry.

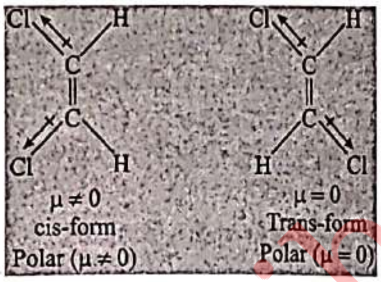
(II) To calculate % ionic character:

$$\% \text{ Ionic character} = \frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100$$

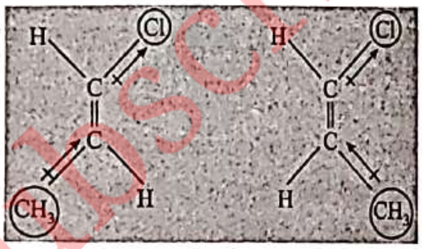
$$= \frac{\mu_{\text{(Observed)}}}{\mu_{\text{(100\% Ionic compound)}}} \times 100$$

(III) To distinguish cis form or trans form:

(*a*) Dipole moment of cis isomer is normally higher than trans isomer.

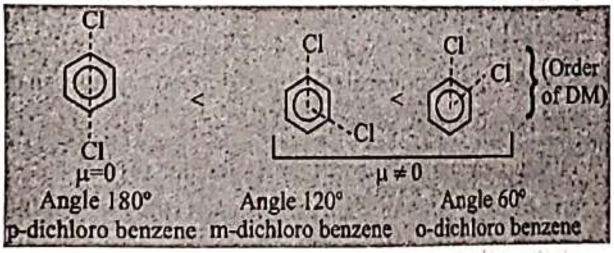
eg. 
Cl
H
C
C
Cl
H
μ≠0
cis-form
Polar (μ≠0)
Cl
H
C
C
H
Cl
μ=0
Trans-form
Polar (μ=0)

(*b*) If two groups have opposite inductive effect then trans-isomer will have greater dipole moment:-

eg. 
H
Cl
C
C
CH3
H
H
Cl
C
C
H
CH3

trans - form (high dipole moment) cis - form (low dipole moment)

(IV) To locate position of substituents in aromatic compounds.

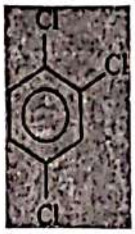

Cl
Cl
μ=0
Angle 180°
p-dichloro benzene
<
Cl
Cl
Angle 120°
m-dichloro benzene
<
Cl
Cl
Angle 60°
o-dichloro benzene
μ≠0
(Order of DM)

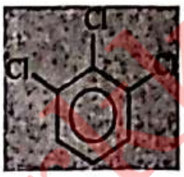
Normally as angle between identical substituents decreases, value of μ increases.

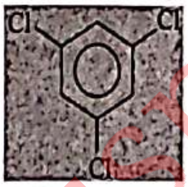
$$\mu \propto \frac{1}{\text{Bond angle}}$$

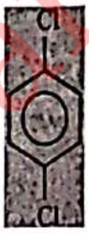
Train Your Brain

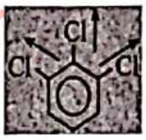
Example 26: Which has maximum dipole moment?

(*a*) 

(*b*) 

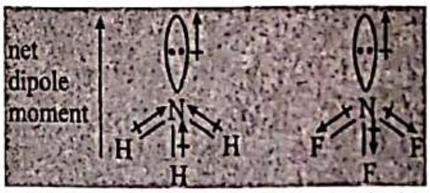
(*c*) 

(*d*) 

Sol. (*b*) Among these,  has maximum dipole moment

Example 27: Why NH_3 is having more dipole moment than NF_3?

Sol. In $\ddot{N}H_3$ molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards. Nitrogen atom but in NF_3 molecule, Fluorine is more electronegative than nitrogen so the net dipole moment is towards fluorine atoms. In NH_3 the bond pair moments and lone pair moments are in the same direction while in NF_3 the lone pair moment and bond pair moments are in opposite direction.


net
dipole
moment
N
H
H
H
N
F
F
F

Example 28: Classify the following bonds as ionic, polar or covalent and give your reasons:

(*a*) Si–Si bond in $Cl_3SiSiCl_3$

(*b*) Si–Cl bond in $Cl_3SiSiCl_3$

(*c*) Ca–F bond in CaF_2

(*d*) N–H bond in NH_3

Sol. (*a*) Covalent, due to same electronegativity.

(*b*) Polar covalent, due to less electronegativity difference.

(*c*) Ionic, due to greater electronegativity difference.

(*d*) Polar covalent, due to different electronegativity.

Example 29: The geometry of SO_3 and its dipole moment are:

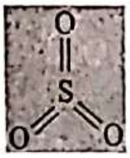
(*a*) pyramidal and non-zero.

(*b*) trigonal planar and non-zero.

(*c*) trigonal planar and zero.

(*d*) T-shaped and zero.

Sol.(*c*)



The steric number of sulphur = 3; so hybridisation is sp^2. There is no lone pair on sulphur atom, therefore according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence the molecule will be symmetrical (trigonal planar) with zero dipole moment

Example 30: Bond length of HCl is 1.275 Å (Charge = 4.8×10^{-10} e.s.u.) if $\mu = 1.02$ D, then HCl is

(*a*) 100% ionic (*b*) 83% covalent

(*c*) 50% covalent (*d*) 40% ionic

Sol. (*b*) $\%\text{ ionic character} = \dfrac{\text{observed}\,\mu}{\text{theoretical}\,\mu} \times 100$

$$= \frac{1.02}{1.275 \times 4.8} \times 100 = 17\%\text{ ionic}$$

$$= 83\%\text{ covalent}$$

Example 31: The dipole moment of the ammonia molecule is 1.48D. The length of the dipole is

(*a*) 3.08×10^{-11} m

(*b*) 5×10^{2} m

(*c*) 308 m

(*d*) None of these

Sol. (*a*) $\mu = 1.48 \times 3.33 \times 10^{-30}$ cm $= 4.93 \times 10^{-30}$ cm.

$q = 1.6 \times 10^{-19}$C

$$\ell = \frac{\mu}{q} = \frac{4.93 \times 10^{-30}}{1.6 \times 10^{-19}} = 3.08 \times 10^{-11}\text{ m}$$

The NH_3 molecule can not have the shape of an equilateral triangle because in this case its dipole moment would be zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

Concept Application

27. Carbon tetrachloride has no net dipole moment because of:

(*a*) Similar electron affinity of C and Cl

(*b*) its regular tetrahedral geometry

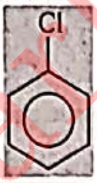
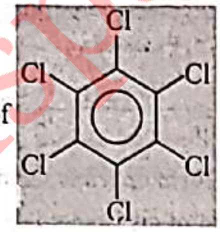
(*c*) its planar geometry

(*d*) similar sizes of C and Cl atoms

28. Which of the following has the least dipole moment?

(*a*) NF_3 (*b*) CO_2

(*c*) SO_2 (*d*) NH_3

29. The dipole moment of  is 1.5 D. The dipole moment of  is:

(*a*) 0 D (*b*) 1.5 D

(*c*) 2.86 D (*d*) 2.25 D

30. Both CO_2 and H_2O contain polar covalent bonds but CO_2 is nonpolar while H_2O is polar because:–

(*a*) H atom is smaller than C atom

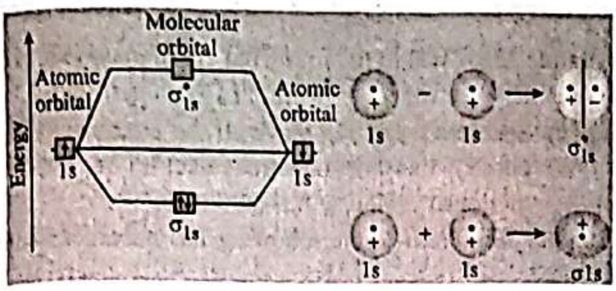
(*b*) CO_2 is a linear molecule while H_2O is an angular molecule

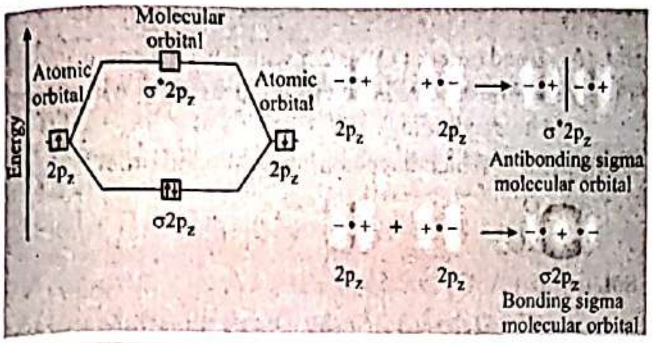
(*c*) O–H bond is more polar than C–H bond

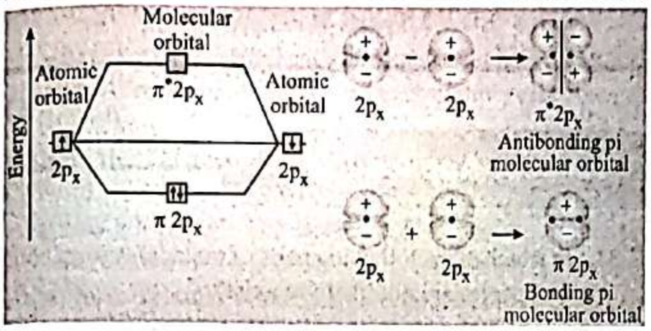
(*d*) CO_2 contains multiple bonds while H_2O has only single bonds

MOLECULAR ORBITAL THEORY (MOT)

- Just like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of nearly equal energies.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. Half of these are called bonding molecular orbital (lower energy) while other half are called antibonding molecular orbital (higher energy).
- Shapes of the molecular orbital depend on the shapes of combining atomic orbitals.
- Filling of electrons in various molecular orbital takes place according to Aufbau, Pauli and Hund's rules for the filling of atomic orbitals.


Molecular orbital
Atomic orbital
σ^*_{1s}
Atomic orbital
Energy
1s
1s
σ_{1s}
1s
1s
σ^*_{1s}
1s
1s
σ1s


Molecular orbital
Atomic orbital
σ*2p_z
Atomic orbital
Energy
2p_z
2p_z
σ2p_z
2p_z
2p_z
σ*2p_z
Antibonding sigma molecular orbital
2p_z
2p_z
σ2p_z
Bonding sigma molecular orbital


Molecular orbital
Atomic orbital
π*2p_x
Atomic orbital
Energy
2p_x
2p_x
π 2p_x
2p_x
2p_x
π*2p_x
Antibonding pi molecular orbital
2p_x
2p_x
π 2p_x
Bonding pi molecular orbital

Linear Combination of Atomic Orbitals (LCAO)

- Molecular orbitals are formed by the linear combination of atomic orbitals i.e. the wave functions of combining atomic orbitals may either be added or may be subtracted.

  $\psi_{(MO)} = \psi_A \pm \psi_B$

  $\psi_{(Bonding)} = \psi_A + \psi_B$; $\psi_{(Antibonding)} = \psi_A - \psi_B$
- A wave possesses a crest and a trough. When orbitals approach in such a way that the crest falls over the crest, a bonding molecular orbital is formed. When the crest of one wave falls over the trough of the other, an antibonding molecular orbital is formed.
- Probability of finding electrons in the bonding molecular orbital is always greater than that of sum of probabilities in the atomic orbitals.

  $\psi_b^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$ and

  $\psi_a^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$
- Bonding molecular orbital are designated as σ, π while the notations for antibonding molecular orbital are σ*, π*

  Bonding molecular orbitals are more stable while antibonding molecular orbitals are less stable.

Conditions for the Formation of Molecular Orbitals

- Combining atomic orbitals should have nearly equal energies.
- Combining atomic orbitals must have proper orientations.

Types of Molecular Orbitals Formed

- **Sigma Molecular Orbitals:** When 1s atomic orbital combines with 1s or 2s combines with 2s, two sigma molecular orbitals are formed. They are marked as bonding (σ) and antibonding (σ*) molecular orbital.
- **π-Molecular Orbitals:** When $2p_x$ combines with $2p_x$ (or $2p_y$ with $2p_y$) two π-molecular orbitals are formed namely bonding (π) and antibonding (π*)

Key Note

By convention, z-axis is taken as internuclear axis, hence when p_z combines with p_z, σp_z and $\sigma^* p_z$ molecular orbitals are formed.

Electronic Configuration and Bond Order for Diatomic Molecules

- Before representing the molecular orbital energy level diagram, we must arrange various orbitals in the order of increasing energy

  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma 2p_z$
- But the order of energy levels of $\sigma 2p_z$ and ($\pi 2p_x = \pi 2p_y$) is reversed for molecular Carbon, Boron, Nitrogen i.e., when total no. of $e^- \leq 14$.

Bond Order (n)

- Bond order is defined as half of the difference between the number of electron present in the bonding and the antibonding molecular orbital.
- Bond order (n) = (1/2) ($N_b - N_a$)
- Molecule is stable only when bond order is positive. If the bond order is negative or zero, the molecule does not exist. It may have whole number as well as fractional values. Higher the value of bond order, greater must be the stability of molecule or molecular ion. Further, higher the bond order, shorter the bond.

  To elaborate certain examples are taken as under

(a) **Hydrogen**

$H_2 : (\sigma 1s)^2$; n = 1

$H_2^+ : (\sigma 1s)^1$; n = 1/2

$H_2^- : (\sigma 1s)^2 ; (\sigma^* 1s)^1$; n= 1/2

This indicates that both H_2 and H_2^+ are stable and H_2 is more stable than H_2^+. Both H_2^+ and H_2^- should be paramagnetic also as they have a half filled molecular orbital.

(b) **Helium**

He_2 does not exist

$He_2 \rightarrow (\sigma 1s)^2, (\sigma^* 1s)^2$; n = 0

But He_2^+ may exist as its bond order will be positive

$He_2^+ \rightarrow (\sigma 1s)^2, (\sigma^* 1s)^1$; n = 1/2

Its stability and bond length is comparable to H_2^+

(c) **Nitrogen**

$N_2 \rightarrow (\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2$: n = 3

High value of bond order (3) implies that it should have highest bond dissociation energy as compared to all other diatomic molecules.

N_2^+ and N_2^- both exhibit bond order 2.5 and are found to be paramagnetic due to the presence of one unpaired electron in both. Stability of these three is in the order $N_2 > N_2^+ > N_2^-$

(d) **Oxygen**

$O_2 - (\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$ Bond order, n= 2

O_2^+ has bond order 2.5 as one electron is removed from the antibonding molecular orbital.

O_2^- has bond order 1.5 as an additional electron is added to the antibonding molecular orbital.

O_2^{2-} has bond order 1.0 as two electrons are added to the two antibonding molecular orbitals.

Stability order (and bond dissociation energy) of the four species are as under.

$O_2^+ > O_2 > O_2^- > O_2^{2-}$

Bond distances are in the reverse order; $O_2^+ < O_2 < O_2^- < O_2^{2-}$

Out of these four species O_2, O_2^+ and O_2^- are paramagnetic due to the presence of 2, 1, 1 unpaired electrons respectively while O_2^{2-} is diamagnetic as it has no unpaired electron.

(*e*) **Fluorine**

Total number of electrons in F_2 molecule is 18 and so it resembles the configuration of O_2^{2-}

$F_2 \rightarrow (\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

Its bond order n is 1 and it is diamagnetic.

(*f*) **Neon**

Ne_2 does not exist as it's bond order comes to be zero.

Key Note

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

Train Your Brain

Example 32: Though O_2 molecule is paramagnetic yet it is a colourless gas. Why?

Sol. It is because the energy gap between HOMO and LUMO levels in O_2 molecule is so large that radiations of visible light cannot excite an e^- from HOMO to LUMO. In fact O_2 gas shows absorption in UV zone. So it is colourless.

Example 33: Correct order of bond energy is:

(*a*) $N_2 > N_2^+ > N_2^- > N_2^{2-}$
(*b*) $N_2^+ > N_2^- > N_2^{2-} > N_2$
(*c*) $N_2 > N_2^- = N_2^+ > N_2^{2-}$
(*d*) $N_2^- > N_2 = N_2^+ > N_2^{2-}$

Sol. (*a*) Bond enregy is directly proportional to the bond order.

Bond order of $N_2 = 3$; N_2^+ & $N_2^- = 2.5$

$N_2^{2-} = 2$

But N_2^- has more electrons in antibonding MO's and thus N_2^+ is more stable than N_2^-. So correct order of bond energy will be $N_2 > N_2^+ > N_2^- > N_2^{2-}$

Example 34: In an antibonding molecular orbital, electron density is minimum-

(*a*) Around one atom of the molecule
(*b*) Between the two nuclei of the molecule
(*c*) At the region away from the nuclei of the molecule
(*d*) at no place

Sol. (*b*) In an antibonding M.O., electron density is minimum between the two nuclei of the molecule.

Example 35: Which of the following are diamagnetic?

(*a*) C_2 (*b*) O_2^{2-} (*c*) Li_2 (*d*) N_2^+

Sol. (*d*) Species C_2, O_2^{2-}, Li_2 have all the electrons paired but N_2^+ has one unpaired electron in bonding molecular orbital so it is paramagnetic.

Example 36: Which of the following has maximum bond strength?

(*a*) O_2 (*b*) O_2^+ (*c*) O_2^- (*d*) O_2^{2-}

Sol. (*b*) Bond order of O_2^+ is 2.5 which is maximum among all the species hence its bond strength will also be the maximum.

Example 37: Which have non-integral bond order?

(*a*) O_2^+
(*b*) O_2^-
(*c*) NO
(*d*) All of these

Sol. (*d*) (*a*) $\therefore$ $O_2^+ = 2.5$

(*b*) $O_2^- = 1.5$

(*c*) $NO = 2.5$

Concept Application

31. In which of the following pairs of molecules/ions, both the species are not likely to exist?
(*a*) H_2^+, He_2^{2-}
(*b*) H_2^-, He_2^{2-}
(*c*) H_2^{2+}, He_2
(*d*) H_2^-, He_2^{2+}

32. When N_2 goes to N_2^+, the N–N bond distance.... and when O_2 goes to O_2^+, the O–O bond distance....
(*a*) Decrease, Increases
(*b*) Increases ,Decrease
(*c*) Increases, Increases
(*d*) None of these

33. In which molecule, last electron is filled in $\sigma 2p_z$?
(*a*) C_2 (*b*) N_2 (*c*) B_2 (*d*) O_2

34. In which of the following set, the value of bond order will be 2.5?
(*a*) O_2^+, NO, NO^{2+}, CN
(*b*) CN, NO^{2+}, CN^-, F_2
(*c*) O_2^+, NO^{2+}, O_2^{2+}, CN^-
(*d*) O_2^{2-}, O_2^-, O_2^+, O_2

35. Among the following which one will have the largest O–O bond length?
(*a*) KO_2
(*b*) O_2
(*c*) $O_2^+[AsF_6]^-$
(*d*) K_2O_2

HYDROGEN BOND

Nitrogen, oxygen and fluorine are highly electronegative elements. When they are bonded to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom attracts nearby any other more electronegative atom having lone pair. This electrostatic force of attraction is called as hydrogen bond and is weaker than covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below :

$$---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}$$

Here, hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, **hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the other electronegative atom (F, O or N) of another or same molecule.**

- Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pairs tend to line up and hold the molecules together.

  Conditions required for H-bond :
  - (*i*) Molecule should have more electronegative atom (F, O, N) linked to H-atom.
  - (*ii*) Size of electronegative atom should be smaller.
  - (*iii*) A lone pair should be present on more electronegative atom.

  Strength of H-bond: The strength of H-bond is usually very low (5 - 10 kJ/mol) but in some cases this value may be as high as 50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also form stronger bonds. The strength of the H-bond can be compared by the relative bond energies.

  $F^- + HF \longrightarrow [FHF]^-$; $\Delta H = -161 \pm 8$ kJ mol^{-1}

  $(CH_3)_2CO + HF \longrightarrow (CH_3)_2CO \ldots\ldots HF$; $\Delta H = -46$ kJ mol^{-1}

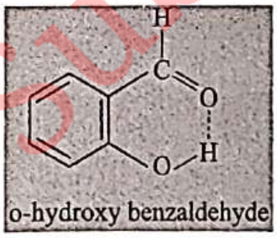
  $H_2O + HOH \longrightarrow H_2O \ldots\ldots HOH$ (ice) ; $\Delta H = -25$ kJ mol^{-1}

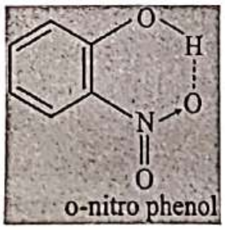
  $HCN + HCN \longrightarrow HCN \ldots\ldots HCN$; $\Delta H = -12$ kJ mol^{-1}

  The magnitude of H-bonding also depends on the physical state of the compounds. H-bonding is maximum in the solid state and minimum in the gaseous state. Thus hydrogen bonds have strong influence on the structure and properties of the compounds.

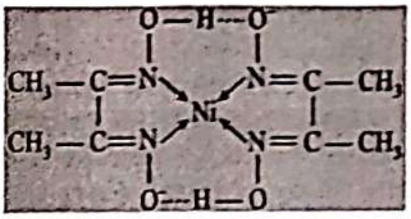
Types of H-Bonds

(*a*) **Intramolecular H-Bonding:** This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.

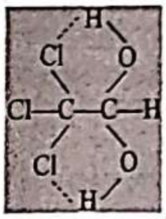
(*a*)

o-hydroxy benzaldehyde

(*b*)

o-nitro phenol

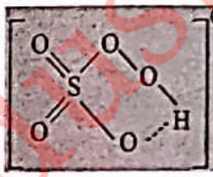
These has lower boiling point (i.e. more volatile) than their para-derivative (where association of molecules takes place using intermolecular H-bonding) because these exists as discrete molecules.

(*c*)

$Ni(DMG)_2$

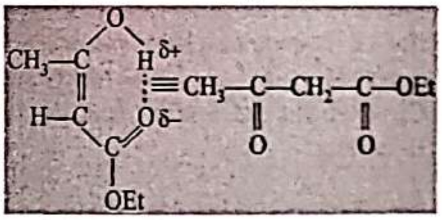
Extra stability of the complex is because of intramolecular hydrogen bonding in addition to the chelating effect.

(*d*)

Chloral hydrate

Chloral hydrate is stable only on account of intramolecular hydrogen bonding.

(*e*)

Persulphate ion (HSO_5^-)

K_1 of peroxomono sulphuric acid (i.e., caro's acid) is greater than K_2. After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult.

(*f*)

Acetoacetic ester (enolic form)

The intramolecular hydrogen bonding attributes the stability of enolic form of aceto acetic ester.

Necessary conditions for the formation of intramolecular hydrogen-bonding:

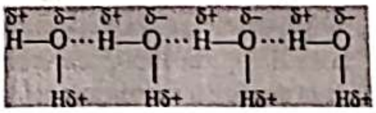
(*a*) The ring formed as a result of hydrogen bonding should be planar.

(*b*) A 5- or 6- membered ring should be formed.

(*c*) Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

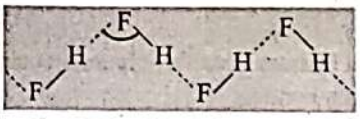
(*b*) **Intermolecular H-Bonding:** When H-bond is formed between two different molecules of the same or different compounds.

(*a*) Due to polar nature of H_2O, there is association of water molecules giving a liquid state of abnormally high boiling point.



- When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this **volume of ice is greater than liquid water and thus ice is lighter than water.** We can say that **density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence, volume increases and hence density decreases. Thus, water has maximum density at 4°C.**

(*b*) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a **zig-zag chain $(HF)_n$** in both the solid and also in the liquid state.

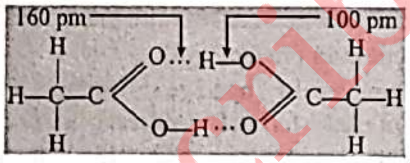


Some hydrogen bonding also occurs in the gas phase, which consists of a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF.

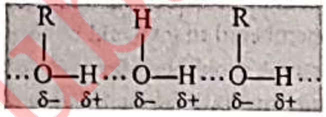
Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $M[HF_2]$; in KHF_2, for example, an X-ray diffraction study together with a neutron diffraction study shows that there is a linear symmetrical anion.

(*c*) There is also similar H-bonding in alcohol (R—OH), ammonia (NH_3) and phenol (C_6H_5OH) molecules.

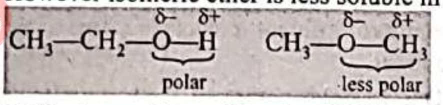
(*d*) Carboxylic acid dimerises in gaseous state due to H-bonding.



(*e*) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and R—OH molecules).

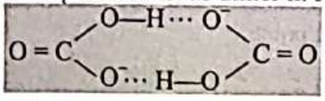


However isomeric ether is less soluble in water.



$$\underbrace{CH_3—CH_2—\overset{\delta-}{O}—\overset{\delta+}{H}}_{\text{polar}} \qquad \underbrace{CH_3—\overset{\delta-}{O}—\overset{\delta+}{CH_3}}_{\text{less polar}}$$

(*f*) HCO_3^- ions exist as dimer in $KHCO_3$



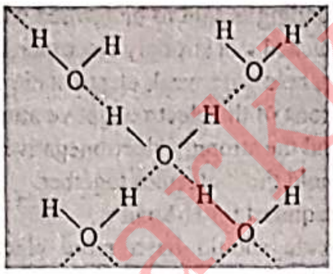
In $Na^+HCO_3^-$, the HCO_3^- ions are linked in to an infinite chain through intermolecular H-bonding.

Train Your Brain

Example 38: Every H_2O molecule is surrounded by maximum how many H_2O molecules?

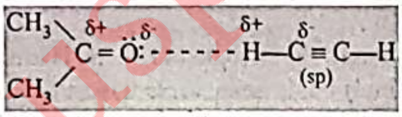
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 6

Sol. (*c*) Each H_2O molecule is surrounded by four other H_2O molecules



Example 39: C_2H_2 is not soluble in H_2O but it is highly soluble in acetone. Explain.

Sol.



In hybridisation, as % s-character increases, electronegativity increases hence C_2H_2 forms H-bonds with O-atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O.

Example 40: Why $SnCl_2.2H_2O$ readily loses one molecule of water at 80°C?

Sol. One water molecule is coordinated to lone pair of electrons on $SnCl_2$ and the other is hydrogen bonded to coordinated water molecules .

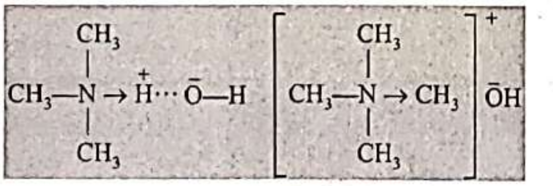
Example 41: Why crystalline sodium peroxide is highly hygroscopic in nature?

Sol. Na_2O_2 forms stable hydrates on account of H-bonding.

$$---O_2^{2-}---(H_2O)_8---O_2^{2-}---(H_2O)_8---$$

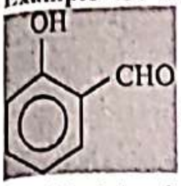
Example 42: Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.

Sol.



In the trimethyl compound, the O–H group is hydrogen bonded to Me_3NH group and this makes it more difficult for the OH group to ionize and hence it is a weak base. In the tetramethyl compound, hydrogen bonding can not occur, so the OH^- group ionizes easily and thus it is a much stronger base.

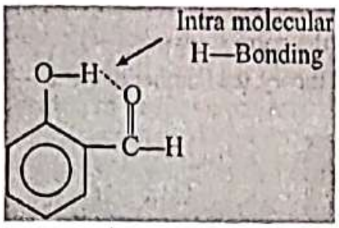
Example 43: Incorrect statement about given compound



is

(*a*) It has intermolecular H-bonding
(*b*) It has intra molecular H-bonding
(*c*) It is steam-volatile
(*d*) None of these

Sol. (*c*)



It is steam-volatile.

Concept Application

36. Which one of the following does not have intermolecular H-bonding?

(*a*) H_2O	(*b*) o-Nitrophenol
(*c*) HF	(*d*) All of these

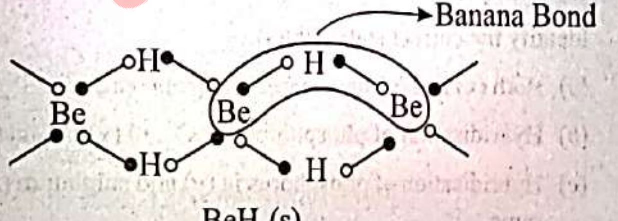
37. Which of the following compounds would have significant intermolecular hydrogen bonding HF, CH_3OH, N_2O_4, CH_4?

(*a*) HF, N_2O_4	(*b*) HF, CH_4, CH_3OH
(*c*) HF, CH_3OH	(*d*) CH_3OH, CH_4

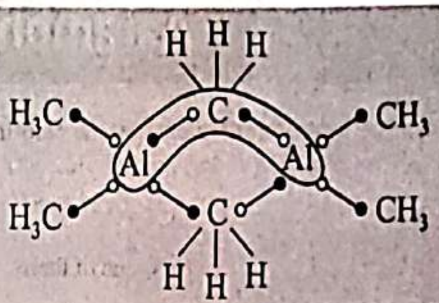
ADVANCED LEARNING

BRIDGE BONDING (ELECTRON DEFICIENT BONDING)

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bond (two centre-two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6, $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.



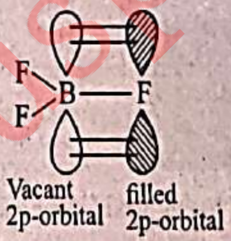
$BeH_2(s)$

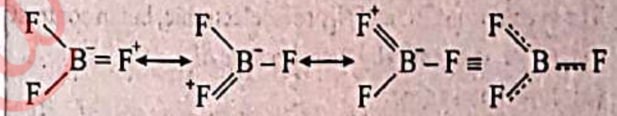


$Al_2(CH_3)_6$

BACK BONDING

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.





Decrease in B – F bond length is due to delocalised pπ–pπ bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

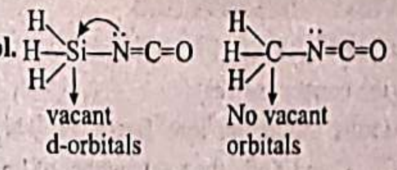
The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows:

$$BF_3 > BCl_3 > BBr_3 > BI_3$$

The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

Example: Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent. Explain.

Sol.



Lone pair on nitrogen is delocalised between N and Si through pπ–dπ back bonding. So silyl isocyanate is linear.

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Aarambh (Solved Examples)

1. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is:

   (*a*) sp^3 (*b*) sp^2

   (*c*) sp (*d*) None of these

Sol. $O-\ddot{\underset{\cdot\cdot}{Cl}}=O$

Bond pair = 2, Lone Pair = 2

Total Electronic pairs = 4 ⇒ Steric no. = 4,

Hybridisation at Cl = sp^3

Therefore, option (*a*) is the correct answer.

2. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3.

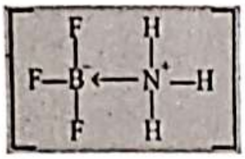
   (*a*) N : tetrahedral, sp^3 ; B: tetrahedral, sp^3

   (*b*) N : pyramidal, sp^3; B: pyramidal, sp^3

   (*c*) N: pyramidal, sp^3; B: planar, sp^2

   (*d*) N: pyramidal, sp^3; B: tetrahedral, sp^3

Sol.



Both 'B' and 'N' has sp^3 hybridisation and tetrahedral geometry.

Therefore, option (*a*) is the correct answer.

3. The cyanide ion CN^- and N_2 are isoelectronic, but in contrast to CN^-, N_2 is chemically inert because of

   (*a*) Low bond energy

   (*b*) Absence of bond polarity

   (*c*) Unsymmetrical electron distribution

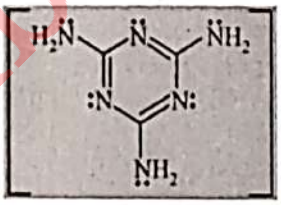
   (*d*) Presence of more number of electron in bonding orbitals

Sol. N_2 is a neutral, non-polar, inert molecule while CN^- is a highly polar, highly reactive ion.

Therefore, option (*b*) is the correct answer.

4. The total number of lone-pair of electrons in melamine is:

Sol. Melamine is a heterocyclic compound.

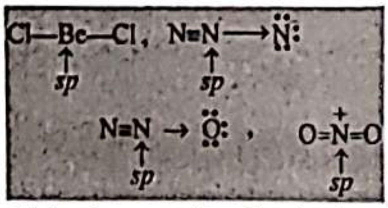


Six lone pairs are present.

Therefore, [6] is the correct answer.

5. Among the triatomic molecules/ions $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecules(s)/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbital(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54].

Sol.

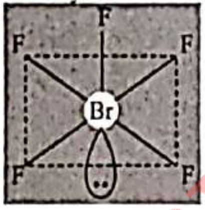


All the above mentioned molecules/ions have sp-hybridised central atom and no Lone pair at central atom, hence linear also.

Therefore, [4] is the correct answer.

6. Based on VSEPR theory, the number of 90° F—Br—F angles in BrF_5 is.

Sol.



To minimize the repulsion, Lone pair would push the Br—F bond pairs in upward direction and all Br—F bond angles will contract.

Therefore, [0] is the correct answer.

7. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of

   (*a*) $Li_2 < Li_2^+ < Li_2^-$ (*b*) $Li_2^- < Li_2^+ < Li_2$

   (*c*) $Li_2 < Li_2^- < Li_2^+$ (*d*) $Li_2^- < Li_2 < Li_2^+$

Sol. $Li_2 = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

$Li_2^+ = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^1$

$$\text{Bond order} = \frac{3-2}{2} = 0.5$$

$Li_2^- = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^1$

$$\text{Bond order} = \frac{4-3}{2} = 0.5$$

Stability order is $Li_2^- < Li_2^+ < Li_2$

(because Li_2^- has more number of electrons in antibonding orbitals which destabilises the species).

Therefore, option (*b*) is the correct answer.

8. Consider the following molecules/anions

   (x) HPO_2F_2 (y) $PO_2F_2^-$

   (z) HSO_3F (t) SO_3F^-

   Identify the correct statement(s).

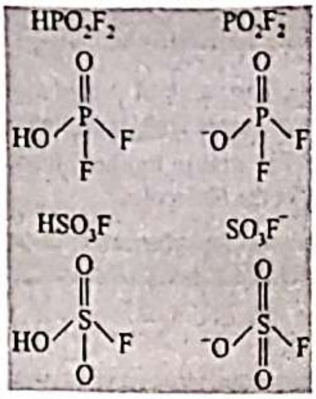
   (*a*) Both (x) and (z) have one –OH group each

   (*b*) Hybridisation of phosphorus in (x) and (y) is same

   (*c*) Hybridisation of phosphorus in (y) and sulphur in (z) is same

   (*d*) Shapes of (x) and (y) are different

Sol. Hybridisation of central atom in all 4 molecules is same.



Therefore, option (*a*, *b*, *c*) is the correct answer.

9. Which of the following set of species are non-polar and hybridisation of central atom is sp^3d?

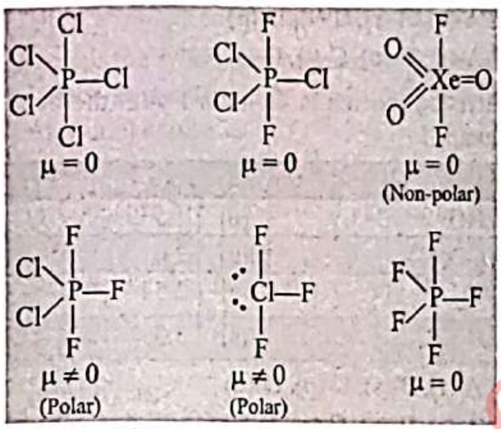
(*a*) PCl_5, PCl_3F_2, XeO_3F_2

(*b*) PCl_5, PCl_2F_3, XeO_2F_2

(*c*) PCl_3F_2, SbF_5, PF_5

(*d*) ClF_3, SF_2Cl_3, XeO_3F_2

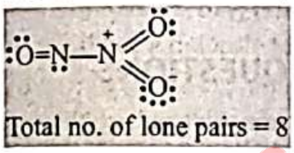
Sol. For non-polar species, dipole moment is zero.



Therefore, option (*a*, *c*) is the correct answer.

10. The total number of lone pairs of electrons in N_2O_3 is:

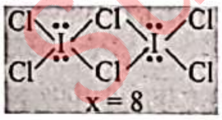
Sol.



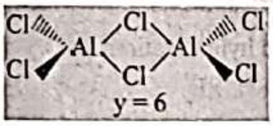
Therefore, [8] is the correct answer.

11. In the structure of I_2Cl_6 and Al_2Cl_6, the maximum number of atoms lying on a plane are x and y respectively. Find the value of x–y.

Sol. I_2Cl_6 is planar



Al_2Cl_6



Therefore, [2] is the correct answer.

12. Which is/are correct regarding P_4?

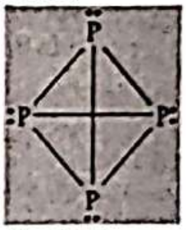
(*a*) It has sp^3 hybridised P

(*b*) There are 4 P – P bonds

(*c*) P – P – P bond angle is 100°

(*d*) There are four lone pairs per molecule

Sol. Each P is sp^3 hybridised.



Therefore, option (*a*, *d*) is the correct answer.

13. Which of the molecule out of B_2 and C_2 has a higher energy of dissociation into atoms? compare the magnetic properties of these molecules.

Sol. B_2 is paramagnetic and C_2 is diamagnetic also C_2 has higher bond order, so C_2 has higher energy of dissociation into atoms.

14. N_2 and O_2 are converted to monocations N_2^+ and O_2^+ respectively, which of the following is wrong statement?

(*a*) In N_2^+, the N—N bond weakens

(*b*) In O_2^+, the O—O bond order increases

(*c*) In O_2^+, the paramagnetism decreases

(*d*) N_2^+ becomes diamagnetic

Sol.

	Bond order	**Unpaired**	**Nature**
N_2	3	0	Diamagnetic
N_2^+	2.5	1	Paramagnetic
O_2	2	2	Paramagnetic
O_2^+	2.5	1	Paramagnetic

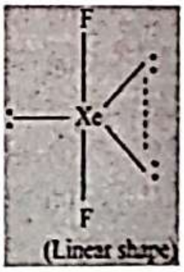
Therefore, option (*d*) is the correct answer.

15. Which does not have "sp" hybridized central atom?

(*a*) XeF_2 (*b*) C_2H_2

(*c*) CO_2 (*d*) BeH_2

Sol. Xe F_2 = sp^3d



Therefore, option (*a*) is the correct answer.

16. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order -

(*a*) $NH_2^- > NH_3 > NH_4^+$ (*b*) $NH_4^+ > NH_3 > NH_2^-$

(*c*) $NH_3 > NH_2^- > NH_4^+$ (*d*) $NH_3 > NH_4^+ > NH_2^-$

Sol. NH_3, NH_4^+ and NH_2^- each have sp^3 hybridization and lone pairs 1, 0 and 2 respectively so bond angle

$NH_4^+ > NH_3 > NH_2^-$

Therefore, option (*b*) is the correct answer.

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. Which of the following has highest ionic character?
   (*a*) $MgCl_2$ (*b*) $CaCl_2$
   (*c*) $BaCl_2$ (*d*) $BeCl_2$
2. The molecule that deviates from octet rule is
   (*a*) NaCl (*b*) $BeCl_2$
   (*c*) MgO (*d*) NH_3
3. Molecule having maximum number of covalent bonds is:
   (*a*) NH_4OH (*b*) NH_4Cl
   (*c*) $CO(NH_2)_2$ (*d*) CH_3OH
4. The correct sequence of decrease in the bond angles of the following hydrides is
   (*a*) $NH_3 > PH_3 > AsH_3 > SbH_3$
   (*b*) $NH_3 > AsH_3 > PH_3 > SbH_3$
   (*c*) $SbH_3 > AsH_3 > PH_3 > NH_3$
   (*d*) $PH_3 > NH_3 > AsH_3 > SbH_3$
5. The correct order towards bond angle is
   (*a*) Bond angle does not depend on hybridisation
   (*b*) $sp < sp^2 < sp^3$
   (*c*) $sp^2 < sp < sp^3$
   (*d*) $sp^3 < sp^2 < sp$
6. The shape of covalent molecule AX_3 is.
   (*a*) Triangular (*b*) T-shape
   (*c*) Pyramidal (*d*) Any of the above
7. Which of the following species given below have shape similar to $XeOF_4$?
   (*a*) XeO_3 (*b*) IOF_4^+
   (*c*) PCl_5 (*d*) XeF_5^+
8. The hybrid state of C in CS_2 should be:
   (*a*) sp^2 (*b*) sp
   (*c*) sp^3 (*d*) Not specific

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
(*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
(*c*) Assertion is True but the Reason is False.
(*d*) Assertion is False but Reason is True.

9. **Assertion:** Geometry of NH_3 molecule is tetrahedral.
   Reason: Nitrogen is sp^3 hybridized in NH_3
10. **Assertion:** The value of dipole moment helps to predict whether a molecule is polar or nonpolar.
    Reason: The dipole moment also helps to predict the geometry of the molecules.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the species in Column-I with the geometry/shape in Column-II.

	Column-I		Column-II
A.	H_3O^+	(p)	Linear
B.	$HC \equiv CH$	(q)	Angular
C.	ClO_2^-	(r)	Tetrahedral
D.	NH_4^+	(s)	Triogonal bipyramidal
		(t)	Pyramidal

   (*a*) A-(p), B-(q), C-(t), D-(r)
   (*b*) A-(t), B-(p), C-(q), D-(r)
   (*c*) A-(s), B-(r), C-(t), D-(p)
   (*d*) A-(r), B-(p), C-(t), D-(s)

12. Match the species in Column-I with the bond order in Column-II.

	Column-I		Column-II
A.	NO	(p)	1.5
B.	CO	(q)	2.0
C.	O_2^-	(r)	2.5
D.	O_2	(s)	3.0

   (*a*) A-(r), B-(s), C-(p), D-(q)
   (*b*) A-(s), B-(p), C-(q), D-(r)
   (*c*) A-(s), B-(r), C-(q), D-(p)
   (*d*) A-(r), B-(p), C-(q), D-(s)

SHORT ANSWER TYPE QUESTIONS

13. Using the valence shell electron pair repulsion theory, predict the shapes of
    (*i*) H_2S (*ii*) PCl_3
14. (*a*) What characterizes a nonpolar covalent bond, and can you give an example of a substance that exhibits this type of bonding?
    (*b*) Calculate the formal charge of each O in ozone.
15. (*a*) "Why does hydrogen sulfide (H_2S) exist as a gas, whereas water (H_2O) is in a liquid state at room temperature?"
    (*b*) Explain s-s and p-p overlapping.
16. Determine the structures and hybridizations of
    (*a*) $BeCl_2$ (*b*) SF_6
    (*c*) BrF_5
17. (*a*) Draw and explain the Lewis structure of nitrite ion.
    (*b*) Compare the dipole moments of NH_3 and NF_3.

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18. (*a*) Explain the reason behind the smaller bond angle in water as compared to ammonia, despite both molecules having distorted tetrahedral geometries.

(*b*) Based on lattice enthalpy and other considerations, arrange the given below species in increasing order of melting point.

RbCl, LiCl, KCl, NaCl

LONG ANSWER TYPE QUESTIONS

19. (*a*) In addition to having a tetrahedral structure, CH_4 might also have a square planar structure, with the C atom in the middle and the four H atoms arranged at the corners. Explain why CH_4 is not square planar?

(*b*) Why does the BeH_2 molecule exhibit a dipole moment of zero, even though its Be—H bonds are polar in nature?

20. (*a*) Define hydrogen bonding and explain why compounds like carboxylic acids, HF, and NH_3, which exhibit hydrogen bonding, have significantly higher melting and boiling points compared to similar compounds without hydrogen bonds. Use examples to illustrate.

(*b*) Show intramolecular H-bonding in o-nitrophenol.

21. (*a*) Explain the hybridization process in PCl_5 and the reason for the longer length of axial bonds as compared to equatorial bonds.

(*b*) Determine which of the following compounds, C_2H_2 or C_2H_4, has the highest total number of sigma and pi bonds.

22. (*a*) Despite the fact that both CO_2 and H_2O are triatomic molecules, the H_2O molecule is bent whereas the CO_2 molecule is linear. On the basis of the dipole moment, explain this.

(*b*) Among water and dimethyl ether (CH_3–O–CH_3), which molecule has a larger bond angle despite having the same central oxygen atom with the same hybridization? Provide a rationale for your answer.

23. (*a*) Draw the Lewis structures for HNO_2, NO_2, and H_2SO_4, indicating the formal charges on each atom in the molecules.

(*b*) Using molecular orbital theory, explain the differences in bond strength and magnetic properties between O_2^+, O_2^- and O_2^{2-} ions.

CASE STUDY BASED QUESTIONS

24. Chemical bonding is a fundamental concept in chemistry that underpins the formation of molecules and compounds. It explains how atoms interact with one another to achieve stability and attain a lower energy state. There are primarily three types of chemical bonds: covalent, ionic, and metallic. In covalent bonds, atoms share electrons to complete their outer electron shells, forming molecules with distinct properties. Ionic bonds involve the transfer of electrons from one atom to another, creating oppositely charged ions that attract each other. Metallic bonding, on the other hand, is characterized by a "sea of electrons" that move freely among metal ions, giving metals their unique properties such as malleability and electrical conductivity. Understanding chemical bonding is essential for predicting chemical reactions, designing materials, and comprehending the structure of matter.

(i) What is the defining characteristic of metallic bonding?

(*a*) Transfer of electrons between atoms
(*b*) Sharing of electrons to complete outer shells
(*c*) A "sea of electrons" moving among metal ions
(*d*) Formation of oppositely charged ions

(ii) Which type of chemical bond involves the transfer of electrons from one atom to another?

(*a*) Covalent (*b*) Ionic
(*c*) Metallic (*d*) Hydrogen

(iii) What unique properties do metals exhibit due to metallic bonding?

(*a*) High melting points and brittleness
(*b*) Low electrical conductivity and solubility
(*c*) Malleability and electrical conductivity
(*d*) Strong covalent bonds and low density

(iv) How do covalent bonds differ from ionic bonds in terms of electron interaction?

(*a*) Covalent bonds involve the transfer of electrons, while ionic bonds involve electron sharing.
(*b*) Covalent bonds involve electron sharing, while ionic bonds involve the transfer of electrons.
(*c*) Covalent bonds and ionic bonds both involve electron transfer.
(*d*) Covalent bonds and ionic bonds are identical in electron behavior.

Prarambh (Topicwise)

INTRODUCTION, VALENCY

1. The octet rule is not obeyed in-

(*a*) CO_2 (*b*) BCl_3
(*c*) PCl_5 (*d*) Both (*b*) and (*c*)

2. Weakest bond is

(*a*) Ionic bond (*b*) Covalent bond
(*c*) Coordinate bond (*d*) Hydrogen bond

3. Which condition favours the bond formation?

(*a*) Maximum attraction and maximum potential energy
(*b*) Minimum attraction and minimum potential energy
(*c*) Minimum potential energy and maximum attraction
(*d*) None of the above

Ionic Bond

4. Lattice energy of alkali metal chlorides follows the order
   (*a*) LiCl > NaCl > KCl > RbCl > CsCl
   (*b*) CsCl > NaCl > KCl > RbCl > LiCl
   (*c*) LiCl > CsCl > NaCl > KCl > RbCl
   (*d*) NaCl > LiCl > KCl > RbCl > CsCl

5. The electronic configuration of four elements L, P, Q and R are given in brackets
   L($1s^2, 2s^2 2p^4$), Q($1s^2, 2s^2 2p^6, 3s^2 3p^5$)
   P($1s^2, 2s^2 2p^6, 3s^1$), R ($1s^2, 2s^2 2p^6, 3s^2$)
   The formulae of ionic compounds that can be formed between these elements are
   (*a*) L_2P, RL, PQ and R_2Q (*b*) LP, RL, PQ and RQ
   (*c*) P_2L, RL, PQ and RQ_2 (*d*) LP, R_2L, P_2Q and RQ

6. An ionic bond A^+B^- is most likely to be formed when:
   (*a*) The ionization energy of A is high and B has low value of electron affinity
   (*b*) The ionization energy of A is low and B has high value of electron affinity
   (*c*) The ionization energy of A and the electron affinity of B both are high
   (*d*) The ionization energy of A and the electron affinity of B both are low

7. In the given bonds which one is most ionic?
   (*a*) Cs – Cl (*b*) Al – Cl (*c*) C – Cl (*d*) H – Cl

Coordinate Bond

8. A simple example of a coordinate covalent bond is exhibited by
   (*a*) C_2H_2 (*b*) HNC (*c*) NH_3 (*d*) HCl

9. Which of the following does not have a coordinate bond?
   (*a*) SO_2 (*b*) HNO_3 (*c*) H_2SO_3 (*d*) HNO_2

Formal Charge

10. $\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}=N=\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}$
    (I) (II) (III)
    Calculate the formal charge of each of I, II and III nitrogen atom respectively
    (*a*) +1, –1, 0 (*b*) –1, –1, +1
    (*c*) –1, +1, –1 (*d*) 0, –1, –1

VBT (Overlapping and Hybridization)

11. Correct statement regarding this reaction
    $BF_3 + NH_3 \longrightarrow [F_3B \leftarrow NH_3]$ is:
    (*a*) Hybridisation of N is changed
    (*b*) Hybridisation of B is changed
    (*c*) NH_3 act as a lone pair donor
    (*d*) Both (*b*) & (*c*)

12. Which type of overlapping results in the formation of a π bond?
    (*a*) Axial overlapping of s – s orbitals
    (*b*) Lateral overlapping of p – p orbitals
    (*c*) Axial overlapping of p – p orbitals
    (*d*) Axial overlapping of s – p orbitals

13. A sigma bond is formed by the overlap of atomic orbitals of atoms A and B. If the bond is formed along the x-axis, which of the following overlaps is acceptable?
    (*a*) s orbital of A and p_z orbital of B
    (*b*) p_x orbital of A and p_y orbital of B
    (*c*) p_z orbital of A and p_x orbital of B
    (*d*) p_x orbital of A and s orbital of B

14. Amongst ClF_3, BF_3 and NH_3 molecules the one with non-planar geometry is
    (*a*) ClF_3 (*b*) NH_3
    (*c*) BF_3 (*d*) None of these

15. Which is not a characteristic of π-bond?
    (*a*) π-bond is formed when a sigma bond is already formed
    (*b*) π-bond are formed from hybrid orbitals
    (*c*) π-bond may be formed by the overlapping of p-orbitals
    (*d*) π- bond results from lateral overlap of atomic orbital

16. Number of σ and π bonds present in
    $CH_3-CH=CH-C\equiv CH$ are:
    (*a*) $10\sigma, 3\pi$ (*b*) $10\sigma, 2\pi$ (*c*) $9\sigma, 2\pi$ (*d*) $8\sigma, 3\pi$

17. Which molecule is not linear?
    (*a*) BeF_2 (*b*) BeH_2 (*c*) CO_2 (*d*) H_2O

18. Cyanogen, $(CN)_2$, has a ____ shape/structure:
    (*a*) Linear (*b*) Zig-zag
    (*c*) V-shape (*d*) Cyclic

19. Which of the set of species have same hybridisation state but different shapes?
    (*a*) NO_2^+, NO_2, NO_2^- (*b*) ClO_4^-, SF_4, XeF_4
    (*c*) NH_4^+, H_3O^+, OF_2 (*d*) $SO_4^{-2}, PO_4^{-3}, ClO_4^-$

20. In an octahedral structure, the pair of d orbitals involved in sp^3d^2 hybridization is:
    (*a*) d_{xy}, d_{yz} (*b*) $d_{x^2-y^2}, d_{z^2}$
    (*c*) $d_{xz}, d_{x^2-y^2}$ (*d*) d_{z^2}, d_{xz}

21. Molecular shapes of SF_4, CF_4 and XeF_4 are:
    (*a*) The same, with 2, 0 and 1 lone pair of electrons respectively
    (*b*) The same, with 1, 1 and 1 lone pair of electrons respectively
    (*c*) Different with 0, 1 and 2 lone pair of electrons respectively
    (*d*) Different with 1, 0 and 2 lone pair of electrons respectively

22. Which of the following molecules has a square pyramidal structure?
    (*a*) XeO_2F_2 (*b*) $XeOF_2$ (*c*) XeO_3F_2 (*d*) $XeOF_4$

23. Which of the following hybridizations involves d_{xy} orbitals?
    (*a*) sp^3d (*b*) sp^3d^2 (*c*) dsp^2 (*d*) sp^3d^3

VSEPR, Bond Angle, Bond Length, Bond Energy

24. Which species has the maximum number of lone pair of electrons on the central atom?
(*a*) $[ClO_3]^-$ (*b*) XeF_4 (*c*) SF_4 (*d*) $[I_3]^-$

25. Which one in the following is not the resonance structure of CO_2?
(*a*) $O=C=O$ (*b*) $^-O{-}C\equiv O^+$
(*c*) $^+O\equiv C{-}O^-$ (*d*) $O\equiv C{-}O$

26. The correct order of increasing adjacent bond angle in the molecules $BeCl_2$, BCl_3, CCl_4 and SF_6 is:
(*a*) $SF_6 < CCl_4 < BCl_3 < BeCl_2$
(*b*) $BeCl_2 < BCl_3 < CCl_4 < SF_6$
(*c*) $SF_6 < CCl_4 < BeCl_2 < BCl_3$
(*d*) $BCl_3 < BeCl_2 < SF_6 < CCl_4$

27. The correct order of increasing bond length in F_2, N_2, Cl_2 and O_2 is:
(*a*) $N_2 < O_2 < Cl_2 < F_2$ (*b*) $N_2 < O_2 < F_2 < Cl_2$
(*c*) $O_2 < N_2 < Cl_2 < F_2$ (*d*) $N_2 < Cl_2 < O_2 < F_2$

28. XeF_6 is
(*a*) Octahedral (*b*) Distorted octahedral
(*c*) Planar (*d*) Tetrahedral

29. Of the following species the one having a square planar structure is
(*a*) NH_4^+ (*b*) BF_4^- (*c*) XeF_4 (*d*) SCl_4

30. Of the following sets which one does NOT contain isoelectronic species?
(*a*) PO_4^{3-}, SO_4^{2-}, ClO_4^- (*b*) CN^-, N_2, C_2^{2-}
(*c*) SO_3^{2-}, CO_3^{2-}, NO_3^- (*d*) BO_3^{3-}, CO_3^{2-}, NO_3^-

31. An element X forms compounds of formula XCl_3, X_2O_5 and Mg_3X_2 but does not form XCl_5 then X is:
(*a*) Aluminium (*b*) Phosphorus
(*c*) Nitrogen (*d*) Boron

32. The formation of which of the following ions is not possible -
(*a*) $[SiF_6]^{2-}$ (*b*) $[AlF_6]^{3-}$ (*c*) $[BF_4]^-$ (*d*) $[BF_6]^{3-}$

Covalent Character in Ionic Compounds (Fajan's Rule)

33. Which among the following elements has the tendency to form covalent compounds?
(*a*) Ba (*b*) Be (*c*) Mg (*d*) Ca

34. Correct order of covalent character of alkaline earth metal chloride is:
(*a*) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$
(*b*) $BeCl_2 < CaCl_2 < SrCl_2 < MgCl_2$
(*c*) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2$
(*d*) $SrCl_2 > BeCl_2 > CaCl_2 > MgCl_2$

35. Which of the compound is least soluble in water?
(*a*) AgF (*b*) AgCl (*c*) AgBr (*d*) AgI

36. Polarization is the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is correct?
(*a*) Maximum polarization is brought about by a cation of high charge
(*b*) Minimum polarization is brought about by a cation of low radius
(*c*) A large cation is likely to bring about a large degree of polarization
(*d*) A small anion is likely to undergo a large degree of polarization

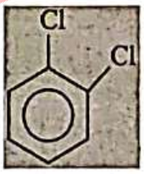
Dipole Moment

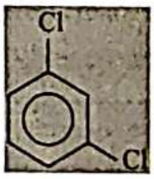
37. Which of the following have both polar and non-polar bonds?
(*a*) C_2Cl_6 (*b*) NH_4Cl
(*c*) HCl (*d*) $AlCl_3$

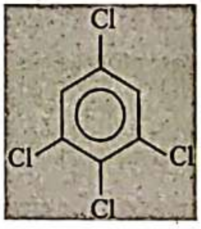
38. Which bond angle θ would result in the maximum dipole moment for the triatomic molecule YXY?
(*a*) $\theta = 90°$ (*b*) $\theta = 120°$
(*c*) $\theta = 150°$ (*d*) $\theta = 180°$

39. The correct order of dipole moment is:
(*a*) $CH_4 < NF_3 < NH_3 < H_2O$
(*b*) $NF_3 < CH_4 < NH_3 < H_2O$
(*c*) $NH_3 < NF_3 < CH_4 < H_2O$
(*d*) $H_2O < NH_3 < NF_3 < CH_4$

40. Which of the following has more dipole moment?

(*a*)


(*b*)


(*c*)


(*d*) All has same dipole moment

41. Zero dipole moment is present in
(*a*) NH_3 (*b*) cis 1, 2-dichloroethene
(*c*) trans 1, 2-dichloroethene (*d*) None of these

42. Which of the following liquids is not deflected by a non-uniform electrostatic field?
(*a*) Water (*b*) Chloroform
(*c*) Nitrobenzene (*d*) Hexane

MOT

43. Which of the following is the correct order of bond-orders of the given species?
(*a*) $O_2^- > O_2^+ > O_2^{2-} > O_2$ (*b*) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(*c*) $O_2^+ > O_2^{2-} > O_2^- > O_2$ (*d*) $O_2^{2-} > O_2 > O_2^+ > O_2^-$

44. Which one is paramagnetic from the following?

(*a*) O_2^- (*b*) NO

(*c*) Both (*a*) and (*b*) (*d*) CN^-

45. Which of the following represents correctly the order of filling of the molecular orbitals of B_2, C_2, N_2?

(*a*) $\pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \dot{\pi}_{2p_y} = \dot{\pi}_{2p_x} < \dot{\sigma}_{2p_z}$

(*b*) $\sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \dot{\pi}_{2p_x} =< \dot{\pi}_{2p_y} < \dot{\sigma}_{2p_z}$

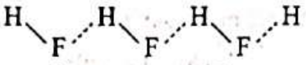
(*c*) $\sigma_{2p_z} = \pi_{2p_x} = \pi_{2p_y} < \dot{\pi}_{2p_x} =< \dot{\pi}_{2p_y} < \dot{\sigma}_{2p_z}$

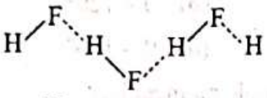
(*d*) $\pi_{2p_x} < \pi_{2p_y} < \sigma_{2p_z} > \dot{\pi}_{2p_y} < \dot{\pi}_{2p_z} = \dot{\sigma}_{2p_z}$

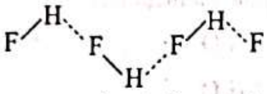
Hydrogen Bonding

46. The H bond in solid HF can be best represented as :

(*a*) H – F....H – F....H – F

(*b*) 

(*c*) 

(*d*) 

47. Contrary to other hydrogen halides, hydrogen fluoride is a liquid at room temperature because

(*a*) Size of F atom is small

(*b*) HF is a weak acid

(*c*) HF molecule are hydrogen bonded

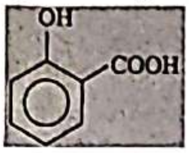
(*d*) Fluorine is highly reactive

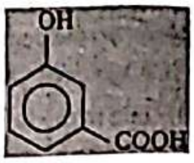
48. The hydrogen bond is strongest in:

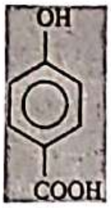
(*a*) O – H - - - S (*b*) S – H - - - O

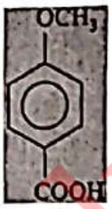
(*c*) F – H - - - F (*d*) O – H - - - O

49. Which of the following has strongest intramolecular hydrogen bonding:

(*a*) 

(*b*) 

(*c*) 

(*d*) 

50. The boiling point of p-nitrophenol is higher than that of o-nitrophenol because:

(*a*) NO_2 group at p-position behaves in a different way from that at o-position

(*b*) Intramolecular hydrogen bonding exists in p-nitrophenol

(*c*) There is intermolecular hydrogen bonding in p-nitrophenol

(*d*) p-nitrophenol has a higher molecular weight than o-nitrophenol

51. Of the following hydrides which has the lowest boiling point?

(*a*) NH_3 (*b*) PH_3 (*c*) SbH_3 (*d*) AsH_3

52. Water has high heat of vaporisation due to

(*a*) Covalent bonding (*b*) H–bonding

(*c*) Ionic bonding (*d*) None of the above

Back Bonding, Bridge Bonding and Odd Electron Molecules

53. In BF_3:

(*a*) B-F bond has some double bond character

(*b*) All the B–F bonds are single covalent in nature

(*c*) Bond energy and bond-length of B–F bond indicate its single bond character

(*d*) All of the above bonds are ionic

Prabal (JEE Main Level)

1. The maximum covalency for representative elements is equal to (excluding 1st and 2nd period):

(*a*) The number of unpaired p-electrons

(*b*) The number of paired d-electrons

(*c*) The number of unpaired s and p-electrons

(*d*) The actual number of s and p-electrons in the outermost shell.

2. The types of bonds present in N_2O_5 are:

(*a*) Only covalent (*b*) Only ionic

(*c*) Ionic and covalent (*d*) Covalent & coordinate

3. Which of the following models best describes the bonding within a layer of the graphite structure?

(*a*) Metallic bonding

(*b*) Ionic bonding

(*c*) Non-metallic covalent bonding

(*d*) Vander Waals force

4. An example of super octet molecule is:

(*a*) SF_6 (*b*) PCl_5 (*c*) IF_7 (*d*) All of these

5. Which of the following species does not contain N – N covalent bond?

(*a*) N_2O_3 (*b*) $N_2O_2^{2-}$ (*c*) N_2O_5 (*d*) N_2O_4

6. Which molecule is T shaped?

(*a*) BeF_2 (*b*) BCl_3 (*c*) NH_3 (*d*) ClF_3

7. The correct order of hybridization of the central atom in the following species NH_3, $PtCl_4^{-2}$, PCl_5 and BCl_3 is

(*a*) dsp^2, sp^3d, sp^2 and sp^3

(*b*) sp^3, dsp^2, sp^3d, sp^2

(*c*) dsp^2, sp^2, sp^3, sp^3d

(*d*) dsp^2, sp^3, sp^2, sp^3d

8. In $ICl_4^{\ominus}$, the shape is square planar. The number of bond pair-lone pair repulsion at 90° are:

(*a*) 6 (*b*) 8 (*c*) 12 (*d*) 4

9. Arrange the following in order of decreasing O–N-O bond angle:

NO_2^+, NO_2^-, NO_3^-

(*a*) $NO_3^- > NO_2^+ > NO_2^-$ (*b*) $NO_3^- > NO_2^- > NO_2^+$

(*c*) $NO_2^+ > NO_3^- > NO_2^-$ (*d*) $NO_2^- > NO_3^- > NO_2^+$

10. Identify the correct match.

A. XeF_2	p. Central atom has sp^3 hybridisation and bent geometry.
B. N_3^-	q. Central atom has sp^3d^2 hybridisation and octahedral.
C. PCl_5(s) anion	r. Central atom has sp hybridisation and linear geometry.
D. I_2Cl_6 (ℓ) cation	s. Central atom has sp^3d hybridisation and linear geometry.

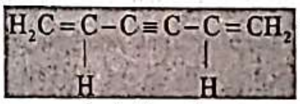
(*a*) A → p; B → q; C → r; D → s

(*b*) A → s; B → q; C → s; D → r

(*c*) A → q; B → r; C → p; D → s

(*d*) A → s; B → r; C → q; D → p

11. Which of the following is **true** statement?

(*a*) All the carbon in 
$H_2C=\underset{H}{C}-C\equiv C-\underset{H}{C}=CH_2$
are in sp^2 hybridisation.

(*b*) In $C_2H_2(CN)_2$ there are six 'σ' bonds.

(*c*) In diamond 'C' is in sp^2 hybridisation.

(*d*) In C_3O_2 all the carbons are in sp hybridisation.

12. Hybridisation of Iodine atoms in ICl_3 (in its stable form, found in solid state) and $I_2Cl_4Br_2$ are:

(*a*) sp^3 & sp^3d^2 (*b*) sp^3d^2 & sp^3d^3

(*c*) Both sp^3d (*d*) Both sp^3d^2

13. In which of the following molecules number of lone pairs and bond pairs on central atom are not equal?

(*a*) H_2O (*b*) I_3^- (*c*) O_2F_2 (*d*) SCl_2

14. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic no. < 21) are

(*a*) pure p (*b*) sp hybrid

(*c*) sp^2 hybrid (*d*) sp^3 hybrid

15. Carbon atoms in $C_2(CN)_4$ are:

(*a*) sp-hybridized (*b*) sp^2-hybridized

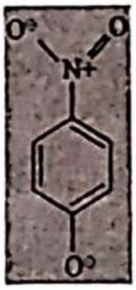
(*c*) sp-and sp^2 hybridized (*d*) sp, sp^2 and sp^3-hybridized

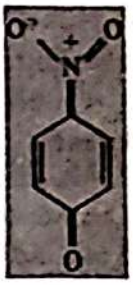
16. In compounds type ECl_3, where E = B, P, As or Bi, the angles Cl - E - Cl for different E are in the order

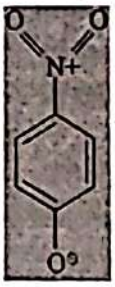
(*a*) B > P = As = Bi (*b*) B > P > As > Bi

(*c*) B < P = As = Bi (*d*) B < P < As < Bi

17. The most likely representation of resonance structure of p-nitrophenoxide is:

(*a*) 

(*b*) 

(*c*) 

(*d*) All of these

18. Which has the smallest bond angle (X – S – X) in the given molecules?

(*a*) OSF_2 (*b*) $OSCl_2$ (*c*) $OSBr_2$ (*d*) OSI_2

19. Which of the following has been arranged in order of decreasing dipole moment?

(*a*) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(*b*) $CH_3F > CH_3Cl > CH_3Br > CH_3I$

(*c*) $CH_3Cl > CH_3Br > CH_3I > CH_3F$

(*d*) $CH_3F > CH_3Cl > CH_3I > CH_3Br$

20. Which of the following molecules are expected to exhibit intermolecular H-bonding?

(I) Acetic acid (II) o-nitrophenol

(III) m-nitrophenol (IV) o-boric acid

(*a*) (I), (II), (III) (*b*) (I), (II), (IV)

(*c*) (I), (III), (IV) (*d*) (II), (III), (IV)

21. The order of strength of hydrogen bonds is:

(*a*) ClH...Cl > NH...N > OH...O > FH...F

(*b*) ClH...Cl < NH...N < OH...O < FH...F

(*c*) ClH...Cl < NH...N > OH...O > FH...F

(*d*) ClH...Cl < NH...N < OH...O > FH...F

22. In which of the dimerisation process, the achievement of the octet is not the driving force?

(*a*) $2AlCl_3 \longrightarrow Al_2Cl_6$ (*b*) $BeCl_2 \longrightarrow BeCl_2$(solid)

(*c*) $2ICl_3 \longrightarrow I_2Cl_6$ (*d*) $2NO_2 \longrightarrow N_2O_4$

23. The molecule not having 3c-2e bond is ....

(*a*) BeH_2 (dimer) (*b*) BeH_2(solid)

(*c*) C_2H_6 (*d*) B_2H_6

24. PCl_5 exists but NCl_5 does not because

(*a*) Nitrogen has no vacant d-orbital

(*b*) NCl_5 is unstable

(*c*) Nitrogen atom is much smaller than p

(*d*) Nitrogen is highly inert

25. Which of the following has a giant covalent structure?
(*a*) Sodium chloride (*b*) Silica
(*c*) Aluminium chloride (*d*) Lead oxide

26. Select correct statement about hydrolysis of BCl_3 and NCl_3
(*a*) NCl_3 is hydroysed and gives HOCl but BCl_3 is not hydrolysed.
(*b*) Both NCl_3 and BCl_3 on hydrolysis gives HCl
(*c*) NCl_3 on hydrolysis gives HOCl but BCl_3 gives HCl.
(*d*) Both NCl_3 and BCl_3 on hydrolysis gives HOCl.

27. Anhydrous $AlCl_3$ is covalent. From the data given below,
Lattice Energy = 5137 kJ/mol.
$\Delta H_{hydration}$ for $Al^{3+} = -4665$ kJ/mol
$\Delta H_{hydration}$ for $Cl^- = -381$ kJ/mol
identify the correct statement.
(*a*) It will remain covalent in aqueous solution
(*b*) The solution will consist of Al^{3+} & Cl^-
(*c*) The solution will consist of hydrated Al^{3+} & Cl^-
(*d*) None of these

28. Least melting point is shown by the compound:
(*a*) $PbCl_2$ (*b*) $SnCl_4$ (*c*) NaCl (*d*) $AlCl_3$

29. The types of bonds present in $CuSO_4\cdot5H_2O$ are:
(*a*) Electrovalent and covalent
(*b*) Electrovalent and coordinate
(*c*) Covalent and coordinate
(*d*) Electrovalent, covalent and coordinate

30. Mg_2C_3 reacts with water forming propyne, C_3^{4-} has
(*a*) Two sigma and two pi bonds
(*b*) Three sigma and one pi bonds
(*c*) Two sigma and one pi bonds
(*d*) Two sigma and three pi bonds

31. Among LiCl, RbCl, $BeCl_2$ and $MgCl_2$, the compounds with the greatest and the least ionic character respectively are:
(*a*) LiCl and RbCl (*b*) RbCl and $BeCl_2$
(*c*) RbCl and $MgCl_2$ (*d*) $MgCl_2$ and $BeCl_2$

32. The correct order of increasing C – O bond length of CO, CO_3^{2-}, CO_2 is
(*a*) $CO_3^{2-} < CO_2 < CO$ (*b*) $CO_2 < CO_3^{2-} < CO$
(*c*) $CO < CO_3^{2-} < CO_2$ (*d*) $CO < CO_2 < CO_3^{2-}$

33. The common features among the species CN^-, CO and NO^+ are
(*a*) Bond order three and isoelectronic
(*b*) Bond order three and weak field ligands
(*c*) Bond order two and π-acceptors
(*d*) Isoelectronic and weak field ligands

34. Which of the following overlaps is **incorrect** [assuming z-axis to be the internuclear axis]?
(*a*) $2p_y + 2p_y \rightarrow \pi 2p_y$ (*b*) $2p_z + 2p_z \rightarrow \sigma 2p_z$
(*c*) $2p_x + 2p_x \rightarrow \pi 2p_x$ (*d*) $1s + 2p_y \rightarrow \pi(1s\text{-}2p_y)$

(*a*) 'A' & 'B' (*b*) 'B' & 'D'
(*c*) only 'D' (*d*) None of these

35. Effective overlapping will be shown by:
(*a*) $\oplus\ominus + \oplus\ominus$ (*b*) $\overset{\oplus}{\ominus} + \overset{\ominus}{\oplus}$
(*c*) $\oplus\ominus + \ominus\oplus$ (*d*) All the above

36. A simplified application of MO theory to the hypothetical 'molecule' OF would give its bond order as
(*a*) 2 (*b*) 1.5 (*c*) 1.0 (*d*) 0.5

37. Which of the following species is paramagnetic?
(*a*) NO^- (*b*) O_2^{2-} (*c*) CN^- (*d*) CO

38. In which of the following processes magnetic moment and Bond order, both are changed.
(*a*) $NO \longrightarrow NO^-$ (*b*) $O_2^+ \longrightarrow O_2^-$
(*c*) $N_2 \longrightarrow N_2^-$ (*d*) All of these

39. According to Molecular orbital theory which of the following is correct?
(*a*) LUMO level for C_2 molecule is σ_{2p_z} orbital
(*b*) In C_2 molecule both the bonds are π bonds
(*c*) In C_2^{2-} ion, there is one σ and two π bonds
(*d*) All the above are correct

40. Which of the following has fractional bond order?
(*a*) O_2^{2+} (*b*) O_2^{2-} (*c*) F_2^{2-} (*d*) H_2^-

INTEGER TYPE QUESTIONS

41. Number of lone pair-bond pair repulsion at 90° are (P) in I_3^-.
Number of lone pair-bond pair repulsion at 90° are (Q) in ICl_4^-.
Find difference of (P) and (Q).

42. Find the total type of different bond lengths observed in PCl_2F_3

43. Consider all the atoms of C_2H_2 are on z-axis. Find total no. of orbitals(s) which involve in overlapping on z-axis

44. How many molecules or ions among the following are linear in shape?
$BeCl_2$ XeF_2 ClF_2^-
I_3^- I_3^+ BF_2^+
$SnCl_2$

45. Find the number of given species where $d_{x^2-y^2}$ orbital participates in hybridisation.
XeF_6 SF_6 IF_7
XeO_3 PCl_5 PF_5

46. Count the total number of unshared electrons on $I_3^- = x$
Count the total number of pπ-dπ bonds in $PO_4^{3-} = y$
Count the total number of lone pairs in $XeF_4 = z$
Hence, find the value of $x - z - y = ?$

47. Find the number of given chemical species which are planar and 'd' orbital of underlined atom participate in hybridisation as well.
$\underline{Sn}Cl_2, \underline{Xe}F_3^{\oplus}, \underline{I}_3^+, \underline{Xe}F_4, \underline{Xe}F_5^+, \underline{I}(CN)_2^{\ominus}$

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. What is the state of hybridisation of Xe in cationic part of solid XeF_6?

   (*a*) sp^3d^3 (*b*) sp^3d^2
   (*c*) sp^3d (*d*) sp^3

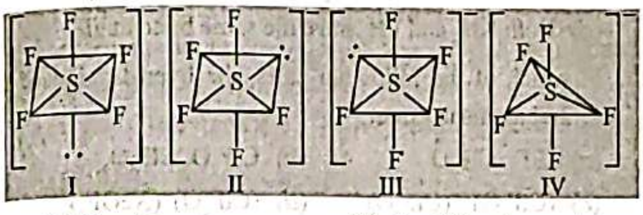
2. KF combines with HF to form KHF_2. The compound contains the species:

   (*a*) K^+, F^- and H^+ (*b*) K^+, F^- and HF
   (*c*) K^+ and $[HF_2]^-$ (*d*) $[KHF]^+$ and F_2

3. Geometry (i.e. arrangement of electron pairs around central atom) of $ClOF_3$ is similar to the:

   (*a*) XeF_4 (*b*) $SOCl_2$
   (*c*) I_3^- (*d*) ClO_4^-

4. The shape of SF_5^- can be:



   (*a*) I only (*b*) I and II only
   (*c*) IV only (*d*) I, II, & III

5. Which of the following statement(s) is/are incorrect?

   (*a*) Ethyne gas is more soluble in acetone than in water.

   (*b*) CH_3F is more polar than CD_3F due to deuterium (D) being less electronegative than hydrogen (H).

   (*c*) Silyl isocyanate (SiH_3NCO) is linear in shape around N while methyl isocyanate (CH_3NCO) is bent in shape around N.

   (*d*) In $CH_2=C=C=C=CH_2$, the 2H–atoms on one C–atom lie in a plane perpendicular to the plane in which 2H–atoms on other C–atom lie.

6. Which of the following compounds contain 3-centered 2-electron bonding?

   (i) $[BeF_2]_n$ (ii) $[Be(CH_3)_2]_n$
   (iii) $[BeCl_2]_n$ (iv) $[BeH_2]_n$

   (*a*) (i) and (ii) (*b*) (ii) and (iii)
   (*c*) (ii) and (iv) (*d*) (iii) and (iv)

7. Which of the following molecule exist?

   (*a*) SH_6 (*b*) HFO_4
   (*c*) FeI_3 (*d*) $HClO_3$

8. Which of the following has the minimum heat of dissociation of N → B bond?

   (*a*) $[(CH_3)_3N \rightarrow BF_3]$ (*b*) $[(CH_3)_3N \rightarrow B(CH_3)F_2]$
   (*c*) $[(CH_3)_3N \rightarrow B(CH_3)_2F]$ (*d*) $[(CH_3)_3N \rightarrow B(CH_3)_3]$

9. Which of the following statements is incorrect?

   (*a*) In ClF_3, the axial Cl—F bond length is longer than equatorial Cl—F bond length.

   (*b*) In SF_4, F–S–F equatorial bond angle is not 120° but 104° due to lp-bp repulsions.

   (*c*) In $[ICl_4]^-$ Cl—I—Cl bond angle is 90°

   (*d*) In OBr_2, the bond angle is less than that in OCl_2.

10. In the structure H_2CSF_4, to decide the plane in which C = S is present the following bond angle value are given

    Axial FSF angle (idealised $= 180°) \Rightarrow 170°$

    Euatorial FSF angle (idealised $= 120°) \Rightarrow 97°$

    After deciding the plane of double bond, which of the following statements is correct?

    (*a*) Two C-H bonds are in the same plane of axial S-F bonds

    (*b*) Two C-H bonds are in the same plane of equatorial S-F bonds.

    (*c*) Maximum five atoms are in the same plane.

    (*d*) Equatorial S-F bonds are perpendicular to plane of π bond.

11. For F_2 and OF molecules consider the following statements:

    I. Bond order for both is one
    II. OF is paramagnetic but F_2 is diamagnetic
    III. F_2 is more likely to dissociate into atoms than OF
    IV. Both have greater number of electrons in BMO than that in AMBO

    Select the correct set of codes using 'T' for true statement and 'F' for incorrect statement in the given sequence.

    (*a*) F T T T (*b*) T F T F
    (*c*) T T T F (*d*) T T F F

12. The correct order of stability for the following species is

    (*a*) $Li_2 < He_2^+ < O_2^+ < C_2$ (*b*) $C_2 < O_2^+ < Li_2 < He_2^+$
    (*c*) $He_2^+ < Li_2 < C_2 < O_2^+$ (*d*) $O_2^+ < C_2 < Li_2 < He_2^+$

13. The order strength of pπ-dπ interaction in the compounds containing bond between Si/P/S/Cl and oxygen is in the order

    (*a*) $P > Si > Cl > S$ (*b*) $Si < P < S < Cl$
    (*c*) $S < Cl < P < Si$ (*d*) $Si > P > S > Cl$

MULTIPLE CORRECT TYPE QUESTIONS

14. Choose the incorrect statements.

    (*a*) CH_3NCS molecule has linear arrangement around N.

    (*b*) SiH_3NCS molecule has linear arrangement around N.

    (*c*) GeH_3NCS molecule has bent arrangement around N.

    (*d*) $[C(SiH_3)_3]^-$ molecule has pyramidal arrangement around C.

15. Select correct option about $C_3N_3Cl_3$ molecule?

(*a*) It is cyclic molecule

(*b*) Geometry at carbon is triangular planar with sp^2 hybridisation of carbon

(*c*) Geometry at nitrogen is triangular planar with sp^2 hybridisation of N

(*d*) Ratio of $\sigma : \pi$: L.P. is 3 : 1 : 4

16. In the following, identify the correct statements?

(*a*) $N_2F_3^+$ is a planar at each nitrogen atom

(*b*) O–F bond length in O_2F_2 is longer than O–F bond length in OF_2.

(*c*) The O–O bond length in O_2F_2 is shorter than O–O bond length in H_2O_2

(*d*) Both nitrogen atoms of $N_2F_3^+$ are sp^2 hybridised

17. The pair of species/molecule having same shape but different hybridisation is/are:

(*a*) XeF_2, CO_2 (*b*) I_3^-, $HgCl_2$

(*c*) BCl_3, SO_3 (*d*) SO_2, OCl_2

18. Which of the following have planar structure?

(*a*) I_3^- (*b*) ICl_3 (*c*) Cl_2O_6 (*d*) Be_2Cl_4

19. Correct order about bond angle is/are :

(*a*) $H_2O > H_2S > H_2Se > H_2Te$

(*b*) $C_2H_2 > C_2H_4 > CH_4 > NH_3$

(*c*) $SF_6 < NH_3 < H_2O < OF_2$

(*d*) $ClO_2 > H_2O > H_2S > SF_6$

20. N_2O has a linear, unsymmetrical structure that may be thought of as a hybrid of two resonance forms. If a resonance form must have a satisfactory Lewis structure, which two of the five structures shown below are the two resonance foms of N_2O?

(*a*) $:N\equiv N=\ddot{O}:$ (*b*) $:\ddot{N}=N=\ddot{O}:$

(*c*) $:\ddot{N}—N\equiv O:$ (*d*) $:N\equiv N—\underset{\cdot\cdot}{\ddot{O}}:$

21. Identify the **correct** option(s).

(*a*) $NH_4^+ > NH_3 > NH_2^-$ (order of bond angle.)

(*b*) $(CH_3)_3B$ is a trigonal planar molecule (not considering the H-atoms on 'C').

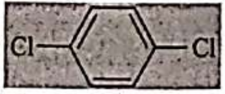
(*c*) In NH_4Cl 'N' atom is in sp^3d hybridisation.

(*d*) In S_8 molecule a total of 16 electrons are left on all the 'S' atoms after bonding.

22. Which has (have) zero value of dipole moment?

(*a*) I_2Cl_6 (*b*) $CHCl_3$

(*c*) CO_2 (*d*)



23. Which of the following statements is/are true for BaO and MgO?

(*a*) BaO is more ionic than MgO

(*b*) MgO is more ionic than BaO

(*c*) BaO has a higher melting point than MgO

(*d*) MgO has a higher melting point than BaO

24. A, B, C are three substances. A does not conduct electricity in the solid, molten state and aqueous solution. B conducts electricity both in the fused and aqueous states, while C conducts electricity only in the aqueous state. In solid state neither B nor C conducts electricity. Which of the following statements is/are true regarding A, B and C?

(*a*) A has polar covalent linkage

(*b*) A has nonpolar covalent linkage

(*c*) B is ionic in nature

(*d*) Cation formed by C is highly polarizing

25. Which of the following have identical bond order?

(*a*) O_2^{2+} (*b*) NO^+

(*c*) CN^- (*d*) CN^+

26. Select the incorrect statement(s) for bond angle:

(*a*) In CF_2 and OF_2, OF_2 has higher bond angle

(*b*) In PF_4^+ and NH_4^+, PF_4^+ has lower bond angle

(*c*) In ClF_3 and BF_3, ClF_3 has lower bond angle

(*d*) Both NH_3 and PH_3 have the same bond angle

27. In which of the following pairs, the hybridisation of the central atoms is same?

(*a*) ClF_3, ClF_3O (*b*) ClF_3O, ClF_3O_2

(*c*) $(ClF_2O)^+$, $(ClF_4O)^-$ (*d*) $(ClF_4O)^-(XeOF_4)$

28. Which of the statement is true for C_3O_2 molecule?

(*a*) Two terminal π-bonds are lying in the same plane

(*b*) Alternate π-bonds are lying in the same plane

(*c*) The ratio of $\sigma : \pi$ bonds is 1 : 1

(*d*) The total number of lone pairs in the molecule is 2.

29. Which of the following is correct statement?

(*a*) Borazine ($B_3N_3H_6$) has higher boiling point as compared to benzene (C_6H_6).

(*b*) The O–O bond length in $O_2[AsF_4]$ is shorter then KO_2.

(*c*) The X-S-X bond angle order is $OSF_2 < OSCl_2 < OSBr_2$

(*d*) None of these

30. Select the correct order of following property

(*a*) Order of energy : $sp^3 > sp^2 > sp$

(*b*) O–N–O bond angle : $NO_3^- > NO_2^+ > NO_2$

(*c*) All bond angles in CH_2F_2 are not identical

(*d*) C–F bond length : $CF_4 > CH_3F > CH_2F_2 > CF_3H$

31. Which of the following statements is/are correct?

(*a*) Out of trimethylamine and trimethylphosphine, trimethylamine has higher dipole moment.

(*b*) Out of $(SiH_3)_2O$ and $(CH_3)_2O$, $(SiH_3)_2O$ is more basic.

(*c*) C–C bond length in C_2 molecule is greater than O–O bond length in O_2 molecule.

(*d*) $N(SiMe_3)_3$ and BF_3 molecules are isostructural about their central atom.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 32 to 34): Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in electronegativity of two atoms. This means that every bond carries with it an electrical moment called the "bond moment". The dipole moment of a molecule is really the vectorial sum of the individual bond moment present in it. To compute the dipole moment it is necessary to find out the values of various bond moment. in the following table dipole moment of different bonds are as given.

Bond :	$\overrightarrow{\text{H—C}}$	$\overrightarrow{\text{C—Cl}}$	$\overrightarrow{\text{C=O}}$
Bond moments :	0.4D	1.5D	2.5D

The group moments of few groups are given:

Group	NO_2	OH	CN	CH_3
Direction of dipole	towards N	towards O	towards N	away from CH_3
Dipole moment	4D	1.6 D	3.8 D	0.4 D

32. The bond angle in H_2S is 97° and its dipole moment is 1.5D. The S – H bond distance is 0.15nm. Therefore approximate percentage ionic character of S – H bond is (neglect the effect of dipole moment of lone pair on sulphur atom in H_2S). (Given [$\cos 97° = -0.12$] and $\sqrt{0.88} = 0.94$)

(*a*) 32 % (*b*) 16 %
(*c*) 84 % (*d*) 10 %

33. In CH_3CCl_3 (I), $CHCl_3$ (II) and CH_3Cl (III) the normal tetrahedral bond angle is maintained. $\left(\cos 70.5° = \frac{1}{3}\right)$ Therefore dipole moments of the given compounds are. (due to – I effect of Cl, the Bond moment of H—C bond are directed toward the H in $CHCl_3$)

(*a*) I = 1.9 D, II = 1.9 D, III = 1.7 D
(*b*) I = 1.9 D, II = 1.7 D, III = 1.9 D
(*c*) I = 1.9 D, II = 1.7 D, III = 1.7 D
(*d*) I = 1.9 D, II = 1.1 D, III = 1.9 D

34. In the acetone molecule considering the normal planar structure, the observed dipole moment of acetone molecule is

(*a*) 2.9 D (*b*) 2.75 D
(*c*) 3 D (*d*) None of these

MATCH THE COLUMN TYPE QUESTIONS

35. Match the species given in column-I with the type of hybridisation given in column-II.

	Column-I		Column-II
A.	$IO_2F_2^-$	p.	sp^3d
B.	F_2SeO	q.	sp^3
C.	$ClOF_3$	r.	sp^2
D.	XeF_5^+	s.	sp^3d^2

(*a*) A → s; B → q; C → p; D → r
(*b*) A → p; B → q; C → p; D → s
(*c*) A → p; B → p; C → q; D → s
(*d*) A → s; B → p; C → q; D → r

36. Match the compounds listed in column-I with characteristic(s) listed in column-II.

	Column-I		Column-II
A.	SF_2	p.	sp^3 and bent
B.	KrF_4	q.	Lone pair(s)
C.	NOCl	r.	Bond angle < 109°28′
D.	$N(Me)_3$	s.	sp^2 and bent
		t.	sp^3d^2 and square planar

(*a*) A → p,q,r; B → q,r,t; C → q,s; D → q,r
(*b*) A → r; B → q,s; C → q,r,t; D → p,q,r
(*c*) A → q,r,s; B → q,s,t; C → p,q,r; D → r,s
(*d*) A → s,r; B → p,q; C → s,t; D → r,s,t

37. Match each Column-I with Column-II and select the correct answer using the code given below the lists.

Column-I		Column-II	
	(Pair of species)		(Identical Property in pairs of species)
A.	PCl_3F_2 & PCl_2F_3	p.	Hybridisation of central atom
B.	BF_3 & BCl_3	q.	Shape of molecule / ion
C.	CO_2 & CN_2^{2-}	r.	μ (dipole moment)
D.	C_6H_6 & $B_3N_3H_6$	s.	Total number of electrons

(*a*) A → p,q; B → p,q,r; C → p,q,r,s; D → p,q,r,s
(*b*) A → p,q,r,s; B → p,q,r; C → p,q; D → p,q,r,s
(*c*) A → p,q,r; B → p,q; C → p,q,r,s; D → p,q,r,s
(*d*) A → p,q,r,s; B → p,q,r; C → p,q,r,s; D → p,q

INTEGER TYPE QUESTIONS

38. Count the total number of X–O bonds having equal bond length in HSO_4^- and $S_3O_6^{2-}$ respectively. (If the answer is 5 and 3 then represent as 53)

39. How many compounds among the following contains N–N bond?

N_2O_3, N_2O_4, N_2O_5. N_2O

40. Find the number of species in which bond angle(s) at central atom is less than idealised bond angle as per hybridisation.

NOF, XeF_4, XeF_3^+, $SbCl_5^{2-}$, IF_2^+, XeF_5^-, O_3, $O(CH_3)_2$

41. Calculate (x + y) for XeO_6^{4-}, where:

x = Total number of 'd' orbitals of xenon atom which participate in bond formation.

y = Number of triangular faces.

42. Consider the following species

$NO_3^-, SO_4^{2-}, ClO_4^-, SO_3, PO_4^{3-}, XeO_3, CO_3^{2-}, SO_3^{2-}$

Then calculate value of |x − y|, where

x : Total number of species which have bond order 1.5 or greater than 1.5

y : Total number of species which have bond order less than 1.5

43. For the following molecules:

$PCl_5, BrF_3, ICl_2^-, XeF_5^-, NO_3^-, XeO_2F_2, PCl_4^+, CH_3^+$

Calculate the value of $\frac{a+b}{c}$

a = Number of species having sp^3d-hybridisation
b = Number of species which are planar
c = Number of species which are non-planar

44. The sum of bond order of O_2, O_2^- and O_2^{2-} is ____.

45. Write sum of the bond order of the following species: C_2^{2-}, B_2, NO, O_2^+, O_2^-, Cl_2, S_2

46. Calculate the % p-character in the orbital occupied by the lone pair in water molecule; [Given: ∠HOH is 104.5° and cos(104.5) = −0.25]

47. Find the ratio of the total number of bonds to the total number of lone pair in $C_3N_3Cl_3$.

48. How many dπ-dπ bonds are present in ClO_3^-?

49. Dipole moment of certain diatomic molecule X–Y is 0.38 D. If the X–Y distance is 158 pm, the percentage of electronic charge developed on X-atom is:

50. Find the number of compounds amongst the following where $d_{x^2-y^2}$ orbitals will not take part in hybridisation.

(1) XeO_6^{4-}
(2) SF_4
(3) $[Cu(NH_3)_4]^{2+}$
(4) $[XeO_3F_2]$
(5) $[XeO_2F_2]$
(6) $POCl_3$
(7) PCl_5

51. How many of the following statements are correct?

(1) Among sp^3d, sp^3d^2 and sp^3d^3 hybridisation, the maximum number of 90° angle between bond pair-bond pair of electrons is observed in sp^3d^2 hybridisation.

(2) Among SF_4, CF_4 and XeF_4, interatomic bond angle of 109°28′ is observed only in SF_4.

(3) Among N_2F_4, N_2F_2 and N_2, the largest N–N bond length is found in N_2F_4.

(4) Among NF_3, NO_3^-, BF_3, H_3O^+ and NH_3; [NF_3, H_3O^+] and [BF_3, NO_3^-] are isostructural pairs.

(5) Among NH_3, PH_3, AsH_3 and SbH_3; SbH_3 has smallest bond angle.

(6) Among $SbCl_3$, $SbBr_3$ and SbI_3, SbI_3 has the largest bond angle.

52. Find the maximum number of atoms lying in the same plane in C_2H_6 molecule.

53. The number of π-bonds lying in the same plane in C_3O_2 is ________.

54. Find total no. of polar molecules.

(a) PF_3Cl_2
(b) SF_4
(c) PCl_5
(d) PCl_3F_2
(e) SF_6
(f) XeF_2
(g) NO_2^+
(h) BF_2Cl
(i) BF_3

55. How many of the following compounds are planar as well as non polar compound:

(a) C_3O_2
(b) $CH_2=C=CH_2$
(c) BF_3
(d) CCl_4
(e) SF_6
(f) XeF_4
(g) IF_5
(h) IF_7
(i) SF_4
(j) ClF_3

PYQ's (Past Year Questions)

KOSSEL LEWIS THEORY & LEWIS DOT STRUCTURE

1. Number of molecules from the following which are exceptions to octet rule is ______. [08 April, 2024 (Shift-I)]
CO_2, NO_2, H_2SO_4, BF_3, CH_4, SiF_4, ClO_2, PCl_5, BeF_2, C_2H_6, $CHCl_3$, CBr_4

2. Which of the following pair of molecules contain odd electron molecule and an expanded octet molecule?
[29 July, 2022 (Shift-I)]
   (*a*) BCl_3 and SF_6 (*b*) NO and H_2SO_4
   (*c*) SF_6 and H_2SO_4 (*d*) BCl_3 and NO

3. Among B_2H_6, $B_3N_3H_6$, N_2O, N_2O_4, $H_2S_2O_3$ and $H_2S_2O_8$, and total number of molecules containing covalent bond between two atoms of the same kind is __________.
[JEE Adv 2019]

IONIC OR ELECTROVALENT BONDING AND COVALENT BONDING

4. Arrange the bonds in order of increasing ionic character in the molecules. LiF, K_2O, N_2, SO_2 and ClF_3.
[01 Feb, 2024 (Shift-I)]
   (*a*) $ClF_3 < N_2 < SO_2 < K_2O < LiF$
   (*b*) $LiF < K_2O < ClF_3 < SO_2 < N_2$
   (*c*) $N_2 < SO_2 < ClF_3 < K_2O < LiF$
   (*d*) $N_2 < ClF_3 < SO_2 < K_2O < LiF$

5. Order of Covalent character: [24 Jan, 2023 (Shift-I)]
   (A) KF > KI; LiF > KF (B) KF < KI; LiF > KF
   (C) $SnCl_4 > SnCl_2$; CuCl > NaCl
   (D) LiF > KF; CuCl < NaCl
   (E) KF < KI; CuCl > NaCl
   (*a*) C, E only (*b*) B, C only
   (*c*) B, C, E only (*d*) A, B only

6. For compound having the formula $GaAlCl_4$, the correct option from the following is [11 April, 2023 (Shift-I)]
   (*a*) Ga is more electronegative than Al and is present as a cationic part of the salt $GaAlCl_4$
   (*b*) Oxidation state of Ga in the salt $GaAlCl_4$ is +3.
   (*c*) Cl forms bond with both Al and Ga in $GaAlCl_4$
   (*d*) Ga is coordinated with Cl in $GaAlCl_4$

7. A hard substance melts at high temperature and is an insulator in both solid and in molten state. This solid is most likely to be a/an [18 March, 2021 (Shift-II)]
   (*a*) Ionic solid (*b*) Metallic solid
   (*c*) Molecular solid (*d*) Covalent solid

BOND PARAMETERS AND VSEPR THEORY

8. Choose the polar molecule from the following:
[27 Jan, 2024 (Shift-I)]
   (*a*) CCl_4 (*b*) CO_2
   (*c*) $CH_2 = CH_2$ (*d*) $CHCl_3$

9. The number of non-polar molecules from the following is __________
HF, H_2O, SO_2, H_2, CO_2, CH_4, NH_3, HCl, $CHCl_3$, BF_3
[27 Jan, 2024 (Shift-II)]

10. The difference in energy between the actual structure and the lowest energy resonance structure for the given compound is
[29 Jan, 2024 (Shift-I)]
    (*a*) Electromeric energy
    (*b*) Resonance energy
    (*c*) Ionization energy
    (*d*) Hyperconjugation energy

11. Number of compounds with one lone pair of electrons on central atom amongst following is:
O_3, H_2O, SF_4, ClF_3, NH_3, BrF_5, XeF_4
[29 Jan, 2024 (Shift-I)]

12. The total number of molecules with zero dipole moment among CH_4, BF_3, H_2O, HF, NH_3, CO_2 and SO_2 is _________.
[29 Jan, 2024 (Shift-II)]

13. Given below are two statements:
Statement-I: Since fluorine is more electronegative than nitrogen, the net dipole moment of NF_3 is greater than NH_3.
Statement-II: In NH_3, the orbital dipole due to lone pair and the dipole moment of NH bonds are in opposite direction, but in NF_3 the orbital dipole due to lone pair and dipole moments of N–F bonds are in same direction.
In the light of the above statements. Choose the most appropriate from the options given below.
[30 Jan, 2024 (Shift-II)]
    (*a*) Statement-I is true but Statement-II is false.
    (*b*) Both Statement-I and Statement-II are false.
    (*c*) Both statement-I and Statement-II is are true.
    (*d*) Statement-I is false but Statement-II is are true.

14. A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1Å, then fractional charge on each atom is ______ $\times 10^{-1}$ esu. (Given $1D = 10^{-18}$ esu cm)
[31 Jan, 2024 (Shift-II)]

15. The number of molecules/ion/s having trigonal bipyramidal shape is ....
PF_5, BrF_5, PCl_5, $[PtCl_4]^{2-}$, BF_3, $Fe(CO)_5$
[01 Feb, 2024 (Shift-I)]

16. Number of compounds/species from the following with non-zero dipole moment is_____ **[04 April, 2024 (Shift-II)]**

$BeCl_2$, BCl_3, NF_3, XeF_4, CCl_4, H_2O, H_2S, HBr, CO_2, H_2, HCl

17. Match List-I with List-II. **[05 April, 2024 (Shift-II)]**

List-I		List-II	
A.	ICl	I.	T-Shape
B.	ICl_3	II.	Square pyramidal
C.	ClF_5	III.	Pentagonal bipyramidal
D.	IF_7	IV.	Linear

Choose the correct answer from the options given below:

(*a*) (A)–(I), (B)–(IV), C–(III), D–(II)

(*b*) (A)–(I), (B)–(III), C–(II), D–(IV)

(*c*) (A)–(IV), (B)–(I), C–(II), D–(III)

(*d*) (A)–(IV), (B)–(III), C–(II), D–(I)

18. Given below are two statements: one is labelled as **Assertion (A)** and the other is labelled as **Reason (R).**

Assertion (A): NH_3 and NF_3 molecule have pyramidal shape with a lone pair of electrons on nitrogen atom. The resultant dipole moment of NH_3 is greater than that of NF_3.

Reason (R): In NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N–H bonds. F is the most electronegative element.

In the light of the above statements, choose the correct answer from the options given below:

[05 April, 2024 (Shift-II)]

(*a*) Both (A) and (R) are true and (R) is the correct explanation of (A)

(*b*) (A) is false but (R) is true

(*c*) (A) is true but (R) is false

(*d*) Both (A) and (R) are true but (R) is NOT the correct explanation of (A)

19. Number of compounds from the following with zero dipole moment is __________. **[05 April, 2024 (Shift-II)]**

HF, H_2, H_2S, CO_2, NH_3, BF_3, CH_4, $CHCl_3$, SiF_4, H_2O, BeF_2

20. Match **List-I** with **List-II**:

List-I (Molecule / Species)		List-II (Property / Shape)	
A.	SO_2Cl_2	I.	Paramagnetic
B.	NO	II.	Diamagnetic
C.	NO_2^-	III.	Tetrahedral
D.	I_3^-	IV.	Linear

Choose the correct answer from the options given below:

[06 April, 2024 (Shift-I)]

(*a*) A-IV, B-I, C-III, D-II (*b*) A-III, B-I, C-II, D-IV

(*c*) A-II, B-III, C-I, D-IV (*d*) A-III, B-IV, C-II, D-I

21. Match **List-I** with **List-II**:

List-I (Hybridization)		List-II (Orientation in Space)	
A.	sp^3	I.	Trigonal bipyramidal
B.	dsp^2	II.	Octahedral
C.	sp^3d	III.	Tetrahedral
D.	sp^3d^2	IV.	Square planar

Choose the correct answer from the options given below:

[06 April, 2024 (Shift-I)]

(*a*) A-III, B-I, C-IV, D-II (*b*) A-II, B-I, C-IV, D-III

(*c*) A-IV, B-III, C-I, D-II (*d*) A-III, B-IV, C-I, D-II

22. Match **List-I** with **List-II**:

List-I (Compound /Species)		List-II (Shape / Geometry)	
A.	SF_4	I.	Tetrahedral
B.	BrF_3	II.	Pyramidal
C.	BrO_3^-	III.	See saw
D.	NH_4^+	IV.	Bent T-shape

Choose the correct answer from the options given below:

[06 April, 2024 (Shift-I)]

(*a*) A-II, B-III, C-I, D-IV (*b*) A-III, B-IV, C-II, D-I

(*c*) A-II, B-IV, C-III, D-I (*d*) A-III, B-II, C-IV, D-I

23. Total number of species from the following with central atom utilising sp^2 hybrid orbitals for bonding is _______.

NH_3, SO_2, SiO_2, $BeCl_2$, C_2H_2, C_2H_4, BCl_3, HCHO, C_6H_6, BF_3, $C_2H_4Cl_2$ **[06 April, 2024 (Shift-II)]**

24. The correct increasing order for bond angles among BF_3, PF_3 and $C\ell F_3$ is: **[09 April, 2024 (Shift-II)]**

(*a*) $PF_3 < BF_3 < C\ell F_3$ (*b*) $BF_3 < PF_3 < C\ell F_3$

(*c*) $C\ell F_3 < PF_3 < BF_3$ (*d*) $BF_3 = PF_3 < C\ell F_3$

25. Consider the following statements:

[15 April, 2023 (Shift-I)]

(A) NF_3 molecule has a trigonal planar structure.

(B) Bond length of N_2 is shorter than O_2.

(C) Isoelectronic molecules or ions have identical bond order.

(D) Dipole moment of H_2S is higher than that of water molecule.

Choose the correct answer from the option below:

(*a*) (A) and (D) are correct

(*b*) (C) and (D) are correct

(*c*) (A) and (B) are correct

(*d*) (B) and (C) are correct

26. **Statement-I:** Dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre.

Statement-II: The crossed arrow of the dipole moment symbolizes the direction of the shift of charges in the molecules. **[25 Jan, 2023 (Shift-II)]**

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) Both Statement-I and Statement-II are correct

(*b*) Statement-I is incorrect but Statement-II is correct

(*c*) Both Statement-I and Statement-II are incorrect

(*d*) Statement-I is correct but Statement-II is incorrect

27. Match List-I with List-II: **[11 April, 2023 (Shift-I)]**

	List - I		List - II
(A)	H_3O^+	(I)	Tetrahedral
(B)	Acetylide anion	(II)	Linear
(C)	NH_4^+	(III)	Pyramidal
(D)	ClO_2^-	(IV)	Bent

Choose the correct answer from the options given below:

(*a*) (A)-(III), (B)-(II), (C)-(I), (D)-(IV)

(*b*) (A)-(III), (B)-(I), (C)-(II), (D)-(IV)

(*c*) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

(*d*) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

28. For OF_2 molecule, consider the following: **[30 Jan, 2023 (Shift-I)]**

(A) Number of lone pairs on oxygen is 2.

(B) FOF angle is less than 104.5°.

(C) Oxidation state of O is -2.

(D) Molecule is bent 'V' shaped.

(E) Molecular geometry is linear.

Correct options are:

(*a*) C, D, E only (*b*) B, E, A only

(*c*) A, C, D only (*d*) A, B, D only

29. Amongst the following, the number of species having the linear shape is _____.

XeF_2, I_3^+, C_3O_2, I_3^-, CO_2, SO_2, $BeCl_2$ and BCl_2^-

[30 Jan, 2023 (Shift-II)]

30. Based upon VSEPR theory, match the shape (geometry) of the molecules in **List-I** with the molecules in **List-II** and select the most appropriate option. **[27 June, 2022 (Shift-I)]**

	List-I (Shape)		List-II (Molecules)
(A)	T-shaped	(I)	XeF_4
(B)	Trigonal planar	(II)	SF_4
(C)	Square planar	(III)	ClF_3
(D)	See-saw	(IV)	BF_3

(*a*) (A)-(I), (B)-(II), (C)-(III), (D)-(IV)

(*b*) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

(*c*) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

(*d*) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

31. Which of the following are isostructural pairs? **[24 Feb, 2021 (Shift-I)]**

A. SO_4^{2-} and CrO_4^{2-} B. $SiCl_4$ and $TiCl_4$

C. NH_3 and NO_3^- D. BCl_3 and $BrCl_3$

(*a*) C and D only (*b*) A and B only

(*c*) A and C only (*d*) B and C only

32. The dipole moments of CCl_4, $CHCl_3$ and CH_4, are in the order **[7 Jan, 2020 (Shift-I)]**

(*a*) $CHCl_3 < CH_4 = CCl_4$ (*b*) $CCl_4 < CH_4 < CHCl_3$

(*c*) $CH_4 = CCl_4 < CHCl_3$ (*d*) $CH_4 < CCl_4 < CHCl_3$

33. The structure of PCl_5 in the solid state is: **[5 Sept, 2020 (Shift-I)]**

(*a*) Tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$

(*b*) Square pyramidal

(*c*) Trigonal bipyramidal

(*d*) Square planar $[PCl_4]^+$ and octahedral $[PCl_6]^-$

34. Among $[I_3]^+$, $[SiO_4]^{4-}$, SO_2Cl_2, XeF_2, SF_4, ClF_3, $Ni(CO)_4$, XeO_2F_2, $[PtCl_4]^{2-}$, XeF_4, and $SOCl_2$, the total number of species having sp^3 hybridised central atom is _____. **[JEE Adv 2023]**

35. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. **[JEE Adv 2019]**

(*a*) $BeCl_2$, CO_2, BCl_3, $CHCl_3$

(*b*) SO_2, C_6H_5Cl, H_2Se, BrF_5

(*c*) BF_3, O_3, SF_6, XeF_6

(*d*) NO_2, NH_3, $POCl_3$, CH_3Cl

36. Consider the following compounds in the liquid form:

O_2, HF, H_2O, NH_3, H_2O_2, CCl_4, $CHCl_3$, C_6H_6, C_6H_5Cl.

When a charged comb is brought near their flowing stream, how many of them show deflection as per the following figure? **[JEE Adv 2019]**

VALENCE BOND THEORY, HYBRIDISATION & MOLECULAR ORBITAL THEORY

37. Sum of bond order of CO and NO^+ is _____. **[27 Jan, 2024 (Shift-I)]**

38. The number of species from the following which are paramagnetic and with bond order equal to one is ____.

H_2, He_2^+, O_2^+, N_2^{2-}, O_2^{2-}, $F_2^{\cdot}$, Ne_2^+, B_2 **[29 Jan, 2024 (Shift-I)]**

39. The total number of molecular orbitals formed from 2*s* and 2*p* atomic orbitals of a diatomic molecule. **[30 Jan, 2024 (Shift-I)]**

40. The linear combination of atomic orbitals to form molecular orbitals takes place only when the combining atomic orbitals

A. have the same energy

B. have the minimum overlap

C. have same symmetry about the molecular axis

D. have different symmetry about the molecular axis

Choose the ***most appropriate*** from the options given below: **[31 Jan, 2024 (Shift-I)]**

(*a*) A, B, C only (*b*) A and C only

(*c*) B, C, D only (*d*) B and D only

41. The number of species from the following in which the central atom uses sp^3 hybrid orbitals in its bonding is________.

NH_3, SO_2, SiO_2, $BeCl_2$, CO_2, H_2O, CH_4, BF_3

[31 Jan, 2024 (Shift-I)]

42. Given below are two tatements:

Statement-I: A π bonding MO has lower electron density above and below the inter-nuclear axis.

Statement-II: The π* antibonding MO has a node between the nuclei.

In the light of the above statements, choose the most appropriate answer from the options given below:

[01 Feb, 2024 (Shift-II)]

(*a*) Both Statement-I and Statement-II are false

(*b*) Both Statement-I and Statement-II are true

(*c*) Statement-I is false but Statement-II is true

(*d*) Statement-I is true but Statement-II is false

43. Number of molecules/species from the following having one unpaired electron is ________. **[04 April, 2024 (Shift-I)]**

O_2, O_2^{-1}, NO, CN^{-1}, O_2^{2-}

44. When Ψ_A and Ψ_B are the wave functions of atomic orbitals, then σ* is represented by: **[08 April, 2024 (Shift-II)]**

(*a*) $\Psi_A - 2\Psi_B$ (*b*) $\Psi_A - \Psi_B$

(*c*) $\Psi_A + 2\Psi_B$ (*d*) $\Psi_A + \Psi_B$

45. The total number of species from the following in which one unpaired electron is present, is _______.

N_2, O_2, C_2^-, O_2^-, O_2^{2-}, H_2^+, CN^-, He_2^+. **[09 April, 2024 (Shift-I)]**

46. Total number of electron present in (π^*) molecular orbitals of O_2, O_2^+ and O_2^- is_______. **[09 April, 2024 (Shift-II)]**

47. What is the number of unpaired electron(s) in the highest occupied molecular orbital of the following species:

$N_2 : N_2^+; O_2; O_2^+$? **[24 Jan, 2023 (Shift-II)]**

(*a*) 0, 1, 2, 1 (*b*) 2, 1, 2, 1

(*c*) 0, 1, 0, 1 (*d*) 2, 1, 0, 1

48. In which of the following processes, the bond order increases and paramagnetic character changes to diamagnetic one?

[13 April, 2023 (Shift-I)]

(*a*) $O_2 \rightarrow O_2^{2-}$ (*b*) $NO \rightarrow NO^+$

(*c*) $N_2 \rightarrow N_2^+$ (*d*) $O_2 \rightarrow O_2^+$

49. Bonding in which of the following diatomic molecule(s) become(s) stronger, on the basis of MO Theory, by removal of an electron? **[25 June, 2022 (Shift-I)]**

(A) NO (B) N_2 (C) O_2

(D) C_2 (E) B_2

Choose the most appropriate answer from the options given below:

(*a*) (A), (B), (C) only (*b*) (B), (C), (E) only

(*c*) (A), (C) only (*d*) (D) only

50. Identify the incorrect statement for PCl_5 from the following

[27 June, 2022 (Shift-II)]

(*a*) In this molecule, orbitals of phosphorous are assumed to undergo sp^3d hybridization

(*b*) The geometry of PCl_5 is trigonal bipyramidal.

(*c*) PCl_5 has two axial bonds stronger than three equatorial bonds

(*d*) The three equatorial bonds of PCl_5 lie in a plane.

51. Match List-I with List-II. **[27 July, 2022 (Shift-II)]**

List-I		List-II	
(A)	$\psi_{MO} = \psi_A - \psi_B$	(I)	Dipole moment
(B)	$\mu = Q \times r$	(II)	Bonding molecular orbital
(C)	$\dfrac{N_b - N_a}{2}$	(III)	Anti-bonding molecular orbital
(D)	$\psi_{MO} = \psi_A + \psi_B$	(IV)	Bond order

Choose the correct answer from the options given below

(*a*) (A)-(II), (B)-(I), (C)-(IV), (D)-(III)

(*b*) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

(*c*) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)

(*d*) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

52. Consider the ions/molecule

$O_2^+, O_2, O_2^-, O_2^{2-}$ **[26 June, 2022 (Shift-I)]**

For increasing bond order the correct option is:

(*a*) $O_2^{2-} < O_2^- < O_2, < O_2^+$ (*b*) $O_2^- < O_2^{2-} < O_2 < O_2^+$

(*c*) $O_2^- < O_2^{2-} < O_2^+ < O_2$ (*d*) $O_2^- < O_2^+ < O_2^{2-} < O_2$

53. Among the following species

N_2, N_2^+, N_2^-, N_2^{2-}, O_2, O_2^+, O_2^-, O_2^{2-},

The number of species showing diamagnetism is ________.

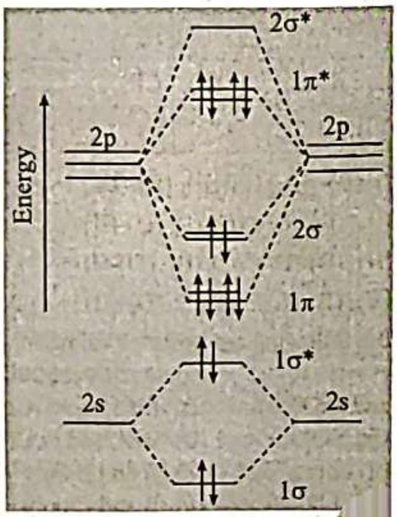
[25 July, 2022 (Shift-I)]

54. The hybridization of P exhibited in PF_5 is sp^xd^y. The value of y is________ **[28 June, 2022 (Shift-I)]**

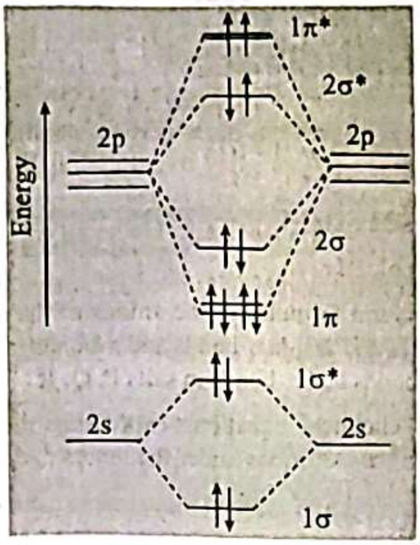
55. AX is a covalent diatomic molecule where A and X are second row elements of periodic table. Based on molecular orbital theory, the bond order of AX is 2.5. The total number of electrons in AX is ____________. (Round off to the nearest integer). **[18 March, 2021 (Shift-I)]**

56. The correct molecular orbital diagram for F_2 molecule in the ground state is **[JEE Adv 2023]**

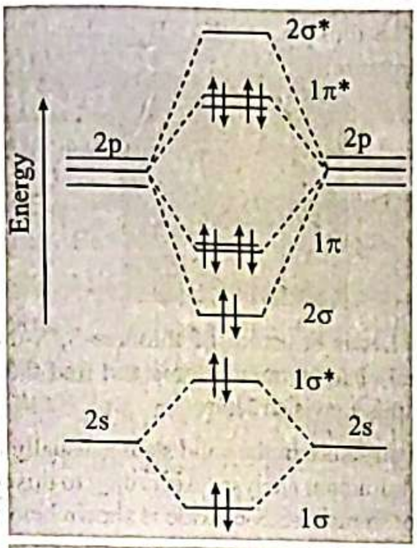
(*a*)



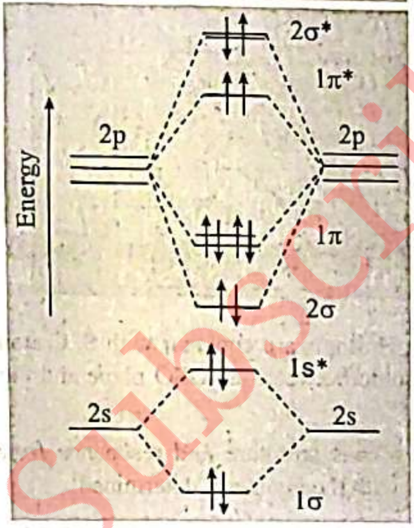
(*b*)



(*c*)



(*d*)



57. For diatomic molecules, the correct statement(s) about the molecular orbitals formed by the overlap of two $2p_z$ orbitals is(are)

(*a*) σ orbital has a total of two nodal planes.

(*b*) σ* orbital has one node in the xz-plane containing the molecular axis.

(*c*) π orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.

(*d*) π* orbital has one node in the xy-plane containing the molecular axis. **[JEE Adv 2022]**

58. At 143 K. the reaction of XeF_4 with O_2F_2, produces a xenon compound **Y**. The total number of lone pair(s) of electrons present on the whole molecule of **Y** is _____. **[JEE Adv 2019]**

59. A tin chloride **Q** undergoes the following reactions (not balanced) **[JEE Adv 2019]**

$Q + Cl^- \rightarrow X$

$Q + Me_3N \rightarrow Y$

$Q + CuCl_2 \rightarrow Z + CuCl$

X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.

Choose the correct option(s).

(*a*) The central atoms in X is sp^3 hybridized

(*b*) The oxidation state of the central atom in Z is +2

(*c*) The central atom in Z has one lone pair of electrons

(*d*) There is a coordinate bond in Y

HYDROGEN BONDING

60. The correct statement/s about Hydrogen bonding is/are : **[04 April, 2024 (Shift-II)]**

A. Hydrogen bonding exists when H is covalently bonded to the highly electro negative atom.

B. Intermolecular H bonding is present in o-nitro phenol

C. Intramolecular H bonding is present in HF.

D. The magnitude of H bonding depends on the physical state of the compound.

E. H-bonding has powerful effect on the structure and properties of compounds.

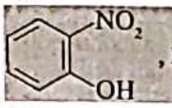
Choose the correct answer from the options given below:

(*a*) A only (*b*) A, D, E only

(*c*) A, B, D only (*d*) A, B, C only

61. Number of molecules from the following which can exhibit hydrogen bonding is ________. (nearest integer)

CH_3OH, H_2O, C_2H_6, C_6H_6



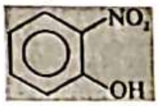
, HF, NH_3

[06 April, 2024 (Shift-I)]

62. Select the compound from the following that will show intramolecular hydrogen bonding. **[01 Feb, 2024 (Shift-II)]**

(*a*) H_2O (*b*) NH_3

(*c*) C_2H_5OH (*d*)



PW Challengers

1. Mark by the "+" in a corresponding window those molecules for which the assertions written on the left side of the Table, are true.

Molecule	Assertion			
	C_2H_4	N_2H_4	H_2O_2	H_2F_2
There is a covalent bond between two equal atoms				
The molecule contains a double bond				
The molecule is planar				
The molecule is polar				
There is also a hydrogen bond in the molecule				
It has basic properties in relation to water				

2. The following assertion and Table are incomplete. Fill in the dotted places by a missing word and the missing formulas, respectively.

Assertion: The electronic structures of the molecules (ions) being placed in the table one under the other are ....

CH_4	C_2H_6	CO_3^{2-}	....	$C_2O_4^{2-}$	....
NH_4^+	$N_2H_6^{2+}$	....	NO_2^+	....	N_2

PASSAGE-I

Compare three salts of a composition $M_2S_2O_x$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

(*a*) The O–O bond is characteristic for the anion.

(*b*) The S–S bond is characteristic for the anion.

(*c*) The S–O–S bond is characteristic for the anion.

(*d*) It is formed by thermal decomposition of hydrogen sulphate.

(*e*) It is formed by anodic oxidation of hydrogen sulphate.

(*f*) It is formed by the reaction of an aqueous solution of sulphite with sulphur.

(*g*) Its aqueous solution dissolves silver bromide.

(*h*) Neutralisation of its aqueous solution with hydroxide MOH yields sulphate M_2SO_4.

(*i*) In aqueous solution, it is able to oxidise Mn(II) salt to permanganate.

Following table indicate the given salt in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

P. $M_2S_2O_p$	b	f	g		
Q. $M_2S_2O_q$	c	d	h		
R. $M_2S_2O_r$	a	e	i		

3. Find the value of p

4. Find the value of q

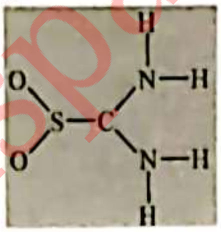
5. Find the value of r

6. Write structural formulas of the anions of the above three salts P, Q, R and assign σ-bonds and π-bonds in them. Find sum of σ-bonds and π-bonds in salts **P, Q, R**

7. Write the chemical equations expressing the processes involved in the assertions under the letters **d, e, f, g, h, i**.

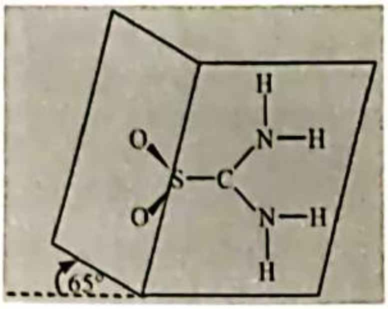
PASSAGE-II

8. Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure



Draw the Lewis structure of thiourea-S, S-dioxide with zero formal charges on all atoms and find the number of π-bond in this Lewis structure.

9. Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is 65°.

Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

IDENTIFY TRUE/FALSE STATEMENTS

10. How many of the following are true statements?

(*a*) CO has much less dipole moment (0.11D) than expected.

(*b*) $SiCl_4$ has abnormally low boiling point than CCl_4

(*c*) Hybridisation in $(CH_3)^+$ is sp^2 but here carbon is pentavalent (*d*) B_2 and C_2 are examples of species having no sigma but only "pi" bonds

(*e*) For CF_3-CF_2-CF_3, two C–F bonds attached to the middle carbon atom are longer as compared to the other C–F bonds at the terminal carbons.

INTEGER TYPE QUESTIONS

11. Find % of s-character of O-H bond in H_2O.

12. If H_2O had no H-bonding, its boiling point would have been .....kelvin.

13. Find % of p-character of C–C bond in cyclopropane having $\angle$C-C-C = 102° (given: cos102° = –0.2079).

14. How many maximum number of atoms are in same plane for CH_2SF_4?

INCREASING/DECREASING ORDER BASED QUESTIONS

15. Which of the following are arranged in correct order?

(*a*) $XeF_2 < XeF_4 < XeF_6$ (Xe-F bond length)

(*b*) Li < Be < B < C < N < O < F < Ne (2nd IE)

(*c*) $CF^+ < CF < CF^-$ (bond order)

(*d*) AlN > GaP > CaO > BaS (LE)

16. Which of the following are arranged in incorrect order?

(*e*) $ClO_2 < ClO_2^{\ominus} < Cl_2O$ (Bond angle)

(*f*) $BF_3 < BF_4^-$ (Bond angle)

(*g*) $BF_3 < BF_4^-$ (Bond length)

(*h*) MeNCS < $(SiH_3)_3NCS$ (basic strength)

17. Which of the following are arranged in correct order?

(*i*) $CHCl_3 < CHF_3$ (acidic strength)

(*j*) $B_2H_6 < C_2H_6$ (acidic strength)

(*k*) $CO < CO^+$ (bond length)

(*l*) Propane < cyclopropane (acidic strength)

18. Which of the following are arranged in correct order?

(*m*) $HF < H_2O < NH_3$ (Boiling point)

(*n*) $HF < H_2O < NH_3$ (Dipole moment)

(*o*) $PF_3 < PH_3$ (Bond angle)

(*p*) $NF_3 < NH_3$ (Bond angle)

19. Which of the following are arranged in correct order?

(*q*) $BF_3 < BCl_3 < BBr_3 < BI_3$ (lewis acidic character)

(*r*) Me_3 C–OH < Me_3 SiOH (acidic character)

(*s*) $Me_3NO < Me_3PO$ (Dipole moment)

(*t*) $ClF_3 < BrF_3$ (Dipole moment)

20. Which of the following are arranged in correct order?

(*u*) $PCl_3F_2 < PF_3Cl_2$ (Dipole moment)

(*v*) $N_2 > O_2 > NO$ (IE)

(*w*) $SF_2 < SF_4 < SF_6$ (Ionic character)

(*x*) $H_2O_2 < F_2O_2$ (O-O bond length)

> *"Strength doesn't come from what you can do. It comes from overcoming the things you once thought you couldn't."*
>
> **– Rikki Rogers**

ANSWER KEY

CONCEPT APPLICATION

1. (d)   2. (d)   3. (d)   4. (a)   5. (d)   6. (d)   7. (b)   8. (b)   9. (d)   10. (a)
11. (a)   12. (c)   13. (a)   14. (c)   15. (d)   16. (a)   17. (b)   18. (c)   19. (b)   20. (b)
21. (c)   22. (b)   23. (b)   24. (c)   25. (c)   26. (a)   27. (b)   28. (b)   29. (a)   30. (b)
31. (c)   32. (a)   33. (b)   34. (a)   35. (d)   36. (b)   37. (c)

SCHOOL LEVEL PROBLEMS

1. (c)   2. (b)   3. (c)   4. (a)   5. (d)   6. (d)   7. (d)   8. (b)   9. (a)   10. (a)
11. (b)   12. (a)   24. (i)-(c), (ii)-(b), (iii)-(c), (iv)-(b)

PRARAMBH (TOPICWISE)

1. (d)   2. (d)   3. (c)   4. (a)   5. (c)   6. (b)   7. (a)   8. (b)   9. (d)   10. (c)
11. (d)   12. (b)   13. (d)   14. (b)   15. (b)   16. (a)   17. (d)   18. (a)   19. (c)   20. (b)
21. (d)   22. (d)   23. (d)   24. (d)   25. (d)   26. (a)   27. (b)   28. (b)   29. (c)   30. (c)
31. (c)   32. (d)   33. (b)   34. (c)   35. (d)   36. (a)   37. (a)   38. (a)   39. (a)   40. (a)
41. (c)   42. (d)   43. (b)   44. (c)   45. (a)   46. (c)   47. (c)   48. (c)   49. (a)   50. (c)
51. (b)   52. (b)   53. (a)

PRABAL (JEE MAIN LEVEL)

1. (d)   2. (d)   3. (c)   4. (d)   5. (c)   6. (d)   7. (b)   8. (b)   9. (c)   10. (d)
11. (d)   12. (d)   13. (b)   14. (c)   15. (c)   16. (b)   17. (a)   18. (a)   19. (a)   20. (c)
21. (b)   22. (c)   23. (c)   24. (a)   25. (b)   26. (c)   27. (c)   28. (b)   29. (d)   30. (a)
31. (b)   32. (d)   33. (a)   34. (c)   35. (c)   36. (b)   37. (a)   38. (d)   39. (d)   40. (d)
41. [2]   42. [3]   43. [6]   44. [5]   45. [3]   46. [3]   47. [3]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (b)   2. (c)   3. (c)   4. (d)   5. (b)   6. (c)   7. (d)   8. (d)   9. (d)   10. (a)
11. (a)   12. (c)   13. (b)   14. (a,d)   15. (a,b,c,d)   16. (a,b,d)   17. (a,b,c,d)   18. (a,b,d)   19. (a,b,d)   20. (b,d)
21. (a,b)   22. (a,c,d)   23. (a,d)   24. (b,c,d)   25. (a,b,c)   26. (a,b,d)   27. (a,b,d)   28. (b,c)   29. (b,c)   30. (a,c)
31. (a,c,d)   32. (b)   33. (d)   34. (a)   35. (b)   36. (a)   37. (a)   38. [36]   39. [3]   40. [5]
41. [10]   42. [0]   43. [3]   44. [4.5]   45. [13.5]   46. [70]   47. [1]   48. [2]   49. [5]   50. [2]
51. [5]   52. [4]   53. [2]   54. [3]   55. [3]

PYQ'S (PAST YEAR QUESTIONS)

1. [6]   2. (b)   3. [4.00]   4. (c)   5. (c)   6. (a)   7. (d)   8. (d)   9. [4]   10. (b)
11. [4]   12. [3]   13. (b)   14. [1.2×10^9]   15. [3]   16. [5]   17. (c)   18. (a)   19. [6]   20. (b)
21. (d)   22. (b)   23. [6]   24. (c)   25. (d)   26. (b)   27. (a)   28. (d)   29. [5]   30. (b)
31. (b)   32. (c)   33. (a)   34. [5]   35. (b,d)   36. [6]   37. [6]   38. [1]   39. [8]   40. (b)
41. [4]   42. (c)   43. [2]   44. (b)   45. [4]   46. [6]   47. (a)   48. (b)   49. (c)   50. (c)
51. (c)   52. (a)   53. [2]   54. [1]   55. [15]   56. (c)   57. (a,d)   58. [19]   59. (a,d)   60. (b)
61. [5]   62. (d)

PW CHALLENGERS

3. [3]   4. [7]   5. [8]   6. [31]   8. [3]   6. [31]   10. [5]   11. [20]   12. [173]   13. [83]
14. [6]   15. (d)   16. (a,b,c,d)   17. (d)   18. (d)   19. (a,b,d)   20. (a,b)